metric studies on chloramine. This investigation was carried out under the sponsorship of the Office of Ordnance Research as one phase of a fundamental study of the synthesis of hydrazine, Contract No. DA-11-022-ORD-828.

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[CONTRIBUTION FROM THE NAVAL ORDNANCE LABORATORY]

# The Limiting Current on a Rotating Disc Electrode in Potassium Iodide–Potassium Triiodide Solutions

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The theory of concentration polarization proposed by B. Levich (1942) for a rotating disc electrode was extended to the ternary system KI–KI$_3$ with KI present in large excess. Using platinum electrodes, the predicted linear relationship between the steady state limiting current and the square root of the angular speed of the disc was verified. These measurements were made at angular speeds such that the critical Reynolds number was not exceeded. The diffusion coefficient of the triiodide ion was calculated from these data.

## Introduction

In a solution with imposed steady state laminar flow conditions, ions are transferred to an electrode by three principal mechanisms: (a) migration, (b) diffusion and (c) convection due to mechanical stirring. At a polarized electrode in such a solution containing an excess of indifferent electrolyte, the current is fixed by the rate of diffusion of the reacting ion species to the electrode. Over a limited voltage range, the current is dependent only on the steady state hydrodynamic stirring conditions which determine the effective thickness of the diffusion boundary layer at the electrode surface.

Equations for the steady state rate of diffusion at a rotating disc electrode have been solved by Levich[1,2] for a binary electrolyte system. In the present study, these equations have been extended to the system KI–KI$_3$, with KI as an indifferent electrolyte. Experimental data have confirmed the relationships derived for this system. The data also have been used to calculate the diffusion coefficient of the triiodide ion.

## Experimental

**Preparation of Materials.**—Boiled, distilled water was used in the preparation of all solutions.

Using reagent grade KI, a 0.1 *N* stock solution was prepared and oxygen removed by bubbling with tank nitrogen which was equilibrated with 0.1 *N* KI prior to introduction into the stock solution. The KI$_3$ complex was obtained by dissolving reagent grade iodine in a concentrated KI solution and diluting so that the resultant solution was 0.1 *N* KI and 0.0601 *N* I$_2$. The water used in preparing the complex was also bubbled with tank nitrogen.

**Apparatus.**—The platinum rotating disc cathode, approximately 2 cm. in diameter, was mounted on a shaft connected to a variable speed motor. The anode consisted of platinum foil whose area was about 20 times that of the cathode and was placed 5 cm. from it. A platinum wire potential probe was positioned near the disc. The vessel containing the electrodes and probe held 600 ml. of electrolyte and was approximately 9 cm. in diameter. Nitrogen was led into the vessel so that a positive pressure was exerted above the electrolyte at all times.

Kinematic viscosity measurements of the 0.1 *N* KI solution at room temperature was made using an Ostwald–Fenske viscometer.[3]

**Procedure.**—Current and voltage measuring apparatus was connected to the electrolysis cell as shown in Fig. 1. Known amounts of iodine complex were added to the KI solution by means of calibrated pipets, and the voltage across the diffusion boundary layer of the cathode was maintained at 0.4 volt for all readings by compensating for the ohmic drop in the solution. Limiting current values were then read for each concentration of iodine complex using various cathode speeds. All measurements were made in a temperature-controlled room.

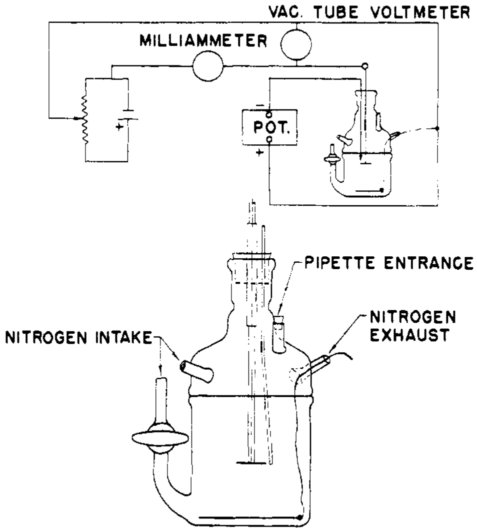

Fig. 1.—Electrolysis cell and circuit connections

## Theoretical

The steady state equation of transfer due to convection, diffusion and migration of ions of type *i* is given by[1]

$$\mathbf{v}\cdot\nabla c_i = D_i\nabla^2 c_i + \frac{n_i e D_i}{kT}\nabla\cdot(c_i\nabla\phi) \qquad (1)$$

where $\mathbf{v}$ is the velocity of convection; $c_i$ is the concentration of ions of type $i$; $D_i$ is the diffusion constant; $n_i$ is the ion valence; $e$ is the unit electronic charge; $k$ is the Boltzmann constant; $T$ is the absolute temperature; $\phi$ is the potential at any point in the electrolyte.

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(1) B. Levich, *Acta Physicochim. U.R.S.S.*, **17**, 257 (1942). Review of the above article by C. W. Tobias, M. Eisenberg and C. R. Wilke, *J. Electrochem. Soc.*, **99**, 359C (1952).

(2) S. Goldstein, "Modern Developments in Fluid Dynamics," Vol. 1, Oxford Press, New York, N. Y. 1938, pp. 110–113.

(3) M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

The condition of electroneutrality in the solution is expressed by

$$\Sigma n_i c_i = 0 \tag{2}$$

In the case of a ternary electrolyte the concentrations of the three ion species may be designated by $c_1 = c_1^\circ + c_1'$, $c_2 = c_2^\circ + c_2'$, and $c_3 = c_3^\circ + c_3'$, where the zero superscripts refer to constant concentrations before electrolysis and the primed quantities to the changes occurring during electrolysis. In a like manner, the potential in the solution may be designated as $\phi = \phi^\circ + \phi'$.

Moreover, if we consider a ternary system in which the reacting ion species (type 3) is present in small amount in comparison with the other two, then equations 1 and 2 become

$$\mathrm{v}\cdot\nabla c_1' = D_1\nabla^2 c_1' + \frac{n_1 e D_1 c_1^\circ}{kT}\nabla^2\phi' \tag{3}$$

$$\mathrm{v}\cdot\nabla c_2' = D_2\nabla^2 c_2' + \frac{n_2 e D_2 c_2^\circ}{kT}\nabla^2\phi' \tag{4}$$

$$\mathrm{v}\cdot\nabla c_3' = D_3\nabla^2 c_3' \tag{5}$$

$$n_1 c_1' + n_2 c_2' + n_3 c_3' = 0 \tag{6}$$

where $c_3^\circ$, $c_1'$, $c_2'$ and $c_3'$ are of the same order of magnitude and are small compared with $c_1^\circ$ and $c_2^\circ$. The migration term in equation 5 has been neglected since this term is exceedingly small in the presence of a supporting electrolyte composed of ions of types 1 and 2.

The solutions of equations 3–6 yield expressions for the current density and potential distribution in the electrolyte. For our purposes, however, an expression for the limiting current may be obtained from the solution of equation 5 and the definition of current density due to a purely diffusive process.

If we assume $c_3' = c_3'(z)$,[1] where $z$ is the normal distance from the disc, then equation 5 becomes

$$v_z\frac{\mathrm{d}c_3'}{\mathrm{d}z} = D_3\frac{\mathrm{d}^2c_3'}{\mathrm{d}z^2} \tag{7}$$

and solving

$$c_3' = a\int_m^z\left(\exp\frac{1}{D_3}\int_0^z v_z\mathrm{d}z\right)\mathrm{d}z + c_3'^{(m)} \tag{8}$$

where $a$ and $c_3'^{(m)}$ are constants of integration. The constant $c_3'^{(m)}$ represents the concentration of the reacting species at $z = m$, in the bulk of the solution.

Since the net current at the cathode surface ($z = 0$) is determined solely by the diffusion of ions of type 3, we can say that the net current density, $j_z = j$, is given by

$$j = 2n_3eD_3\left(\frac{\mathrm{d}c_3'}{\mathrm{d}z}\right)_{z=0} \tag{9}$$

where the cathode reaction is

$$\mathrm{I_3^-} + 2\mathrm{e}^- \longrightarrow 3\mathrm{I}^-$$

From equation 8 we find that $(\mathrm{d}c_3'/\mathrm{d}z)_{z=0} = a$; whence from equation 9

$$a = \frac{j}{2n_3eD_3} \tag{10}$$

Equation 8 then becomes

$$c_3' = \frac{j}{2n_3eD_3}\int_m^z\left(\exp\frac{1}{D_3}\int_0^z v_z\mathrm{d}z\right)\mathrm{d}z + c_3'^{(m)} \tag{11}$$

For the limiting current to occur we must have the following boundary conditions

at $z = 0$, $c_3' = -c_3^\circ$, so that $c_3 = 0$
at $z = m$, $c_3'^{(m)} = 0$, so that $c_3 = c_3^\circ$

Thus, for the limiting current equation 10 becomes at $z = 0$

$$-c_3^\circ = \frac{j_{\mathrm{lim}}}{2n_3eD_3}\int_m^0\left(\exp\frac{1}{D_3}\int_0^z v_z\mathrm{d}z\right)\mathrm{d}z \tag{12}$$

Using the expression for $v_z$ from the hydrodynamic solution,[2] which involves the kinematic viscosity and the angular speed of rotation, Levich[1] evaluated the integral in equation 12 and obtained

$$\int_m^0\left(\exp\frac{1}{D_3}\int_0^z v_z\mathrm{d}z\right)\mathrm{d}z = -0.647\left(\frac{D_3}{\nu}\right)^{1/3}\left(\frac{\nu}{s}\right)^{1/2} \tag{13}$$

where $\nu$ is the kinematic viscosity of the solution and $s$ is the number of r.p.s. of the rotating disc electrode.

Thus we get from equation 12

$$j_{\mathrm{lim}} = \frac{2n_3eD_3c_3^\circ}{0.647(D_3/\nu)^{1/3}(\nu/s)^{1/2}} \tag{14}$$

where the quantity $0.647(D_3/\nu)^{1/3}(\nu/s)^{1/2}$ may be considered as the diffusion boundary layer thickness at the rotating cathode.

Equation 14 may be put into the following form

$$I_{\mathrm{lim}} = \frac{2n_3eD_3^{2/3}(c_3^\circ s^{1/2})A\left(\frac{N}{2}\right)\times 10^{-3}}{0.647\nu^{1/6}} \tag{15}$$

where $N$ is Avogadro's number; $c_3^\circ$ is the concentration of iodine expressed in normality; and $A$ is the area of the cathode surface.

For fitting a regression line by the method of least squares, the product $c_3^\circ s^{1/2}$ may be considered as the independent variable. The regression coefficient is then given by

$$b = \frac{I_{\mathrm{lim}}}{c_3^\circ s^{1/2}} = \frac{n_3eD_3AN}{0.647\nu^{1/6}}\times 10^{-3} \tag{16}$$

from which we can solve for the diffusion coefficient of the triiodide ion

$$D_3 = \left[\frac{0.647\nu^{1/6}b}{n_3eAN}\times 10^3\right]^{3/2} \tag{17}$$

## Results

The flow of fluid dragged by a rotating disc remains laminar up to Reynolds number $Re \sim 10^5$. In the experimental work being presented the value of $Re$ was less than 5000 for all disc speeds.

Table I shows the experimental data for various disc speeds and iodine concentrations. Plots of

TABLE I

LIMITING CURRENTS IN MILLIAMPERES AT 0.4 V. FOR VARIOUS CONCENTRATIONS OF $I_2$ AND VARIOUS CATHODE SPEEDS

| (r.p.s.)$^{1/2}$ | Concn. of $I_2$ in normality × $10^4$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1.99 | 3.97 | 5.93 | 7.89 | 9.83 | 33.1 | 54.6 | 74.5 |
| 1.22 | 0.122 | 0.243 | 0.361 | 0.481 | 0.593 | 2.03 | 3.36 | 4.55 |
| 1.87 | .183 | .367 | .548 | .733 | .904 | 3.08 | 5.08 | 6.87 |
| 2.30 | .228 | .451 | .675 | .901 | 1.13 | 3.80 | 6.27 | 8.51 |
| 3.15 | .309 | .616 | .923 | 1.23 | 1.53 | 5.19 | 8.57 | 11.6 |
| 3.63 | .355 | .709 | 1.07 | 1.42 | 1.78 | 5.96 | 9.82 | 13.2 |
| 4.28 | .418 | .832 | 1.26 | 1.68 | 2.10 | 7.02 | 11.4 | 15.7 |
| 4.73 | .463 | .928 | 1.40 | 1.87 | 2.33 | 7.80 | 12.8 | 17.2 |
| 5.31 | .520 | 1.05 | 1.57 | 2.09 | 2.60 | 8.72 | 14.2 | 19.1 |
| 6.22 | .601 | 1.21 | 1.81 | 2.42 | 3.02 | 10.0 | 16.3 | 21.8 |
| 6.66 | .643 | 1.30 | 1.93 | 2.58 | 3.22 | 10.8 | 17.5 | 22.9 |

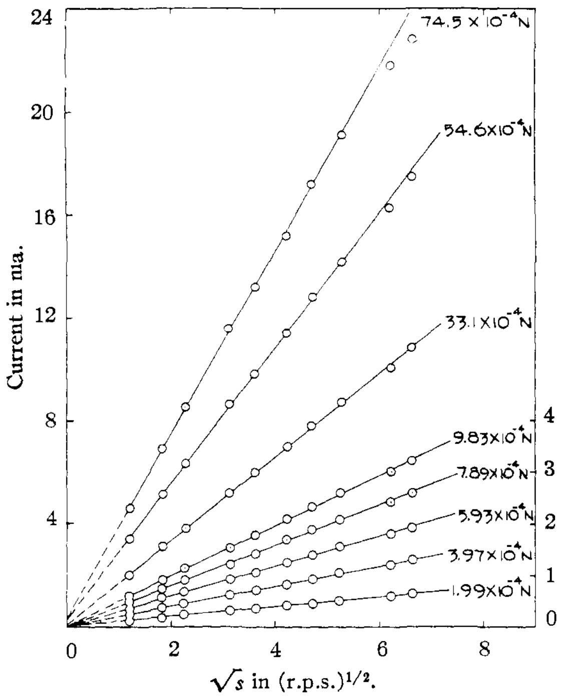

Fig. 2.—The effect of varying disc speed on the limiting current; scale at right applies to lower five plots.

these data are presented in Fig. 2, from which a linear relationship can be seen between the limiting current and the $\sqrt{s}$ for different concentrations of $I_2$. Extrapolations of these lines back to zero speed pass through the origin within experimental error. Figure 3 also shows a linear relationship existing between the limiting current and $I_2$ concentration for different electrode speeds, and extrapolations of these lines back to zero $I_2$ concentration likewise pass through the origin within experimental error.

The fitting of a regression line by least squares to the data in Table I, with $c_3^0 s^{1/2}$ as the independent variable, yielded a calculated value $b = 0.04798 \pm 0.00031$ for the regression coefficient given by equation 16, where the error is expressed to the 5% probability level.[4] The limiting current intercept of the regression line was zero within experimental error.

Measurement of the kinematic viscosity of the solution at room temperature (25.7°) gave $\nu^{25.7} = 0.8679 \pm 0.0025$ centistoke. The viscosity of the solution with density $\rho^{25.7} = 1.0080$ g./cm.$^3$ is therefore $\eta^{25.7} = 0.8748 \pm 0.0025$ centipoise. The area of the disc electrode was measured as 3.0992 ± 0.0059 sq. cm. Calculation of the diffusion coefficient for the triiodide ion from equation 17 gave $D_3 = (1.021 \pm 0.006) \times 10^{-5}$ cm.$^2$/sec. All the errors indicated are expressed to the 5% probability level.[5]

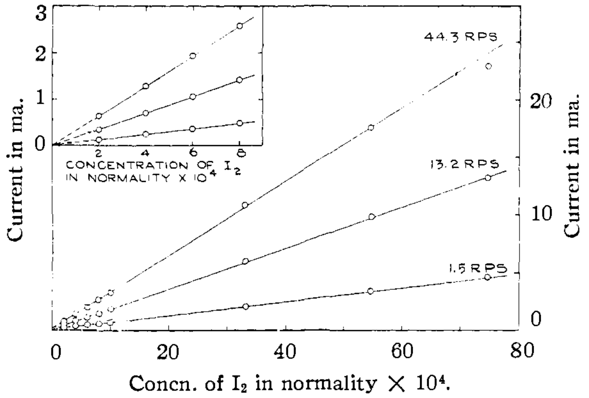

Fig. 3.—The effect of varying concentration of $I_2$ on the limiting current; region near origin is expanded in upper left.

Another independent experimental run at a room temperature of 26.2° gave similar linear relationships. Constants of the solution at this temperature were $\nu^{26.2} = 0.8572 \pm 0.0019$ centistoke, $\rho^{26.2} = 1.0079$ g./cm.$^3$, and $\eta^{26.2} = 0.8640 \pm 0.0019$ centipoise. The regression coefficient was calculated as $b = 0.04861 \pm 0.00046$ and the diffusion coefficient as $D_3 = (1.038 \pm 0.010) \times 10^{-5}$ cm.$^2$/sec.

## Discussion

Other experimental work done by the authors on the deposition of $Cu^{++}$ and $Ag^+$ ions has resulted in positive and negative deviations from the linear relationship between limiting current and $\sqrt{s}$. The deviations were particularly noticeable when the deposits became thick and surface effects became important.

In order to avoid such surface effects the system $KI–KI_3$ with platinum electrodes was chosen. The results indicate that in the absence of electrode surface effects and hydrodynamic turbulence, Levich's steady state laminar theory of concentration polarization is well borne out by the experimental data presented. The data also yielded a value of the diffusion coefficient of the single ionic species $I_3^-$. The values of the diffusion coefficient thus obtained compare favorably with those found by non-electrolytic methods. Edgar and Diggs[6] reported a value of $D_{I_3^-} = 1.08 \times 10^{-5}$ cm.$^2$/sec. for 0.05 *N* $I_2$ in 0.25 *N* KI at 25°.

Experimental verification of the laminar theory also has been given by Siver and Kabanov[7] who employed the reduction of $O_2$ to $H_2O_2$ using an amalgamated copper cathode.

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[4] R. A. Fisher, "Statistical Methods for Research Workers," Oliver and Boyd, London, 1946, p. 135.

[5] R. A. Fisher, *ibid*, p. 122.

[6] G. Edgar and S. H. Diggs, THIS JOURNAL, **38**, 253 (1916).

[7] Y. G. Siver and B. N. Kabanov, *J. Phys. Chem.* (*U.S.S.R.*), **22**, 53 (1948).