PHYSICAL AND INORGANIC CHEMISTRY

The Ratio of the First to the Second Diffusion Current of Oxygen at the Dropping Mercury Electrode. Diffusion Coefficient of Oxygen

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No exaltation of the first oxygen wave in air-saturated solutions is found when stirring of the liquid close to the dropping mercury electrode is eliminated by addition of 0.005% polyacrylamide and when correction is made for the contribution to the current by hydrogen peroxide formed in the reduction. Using as supporting electrolyte tetraethylammonium chloride, prepared by neutralization of the hydroxide, a large apparent exaltation of the first wave is observed. This is due to a volatile impurity formed in the hydroxide solution. No exaltation is found in solutions of the pure tetraalkyl salt. Using Koutecky's value of 39 for B in the modified Ilkovic equation for the maximum value of the diffusion current (i_{max}) an average value of the diffusion coefficient of oxygen at 25° in 0.1 M sodium perchlorate or potassium hydroxide of 1.95×10^{-5} cm.^{2}/sec. is calculated. The value of B in the modified Ilkovic equation for i_{av} depends slightly upon the characteristics of the electrode and the diffusion coefficient of the electroactive species. Using a value of 25 for B for our electrode, calculated values of i_{av}/i_{max} are in close agreement with the experimental values.

Introduction

Oxygen yields two reduction waves at the dropping mercury electrode, the first one corresponding to a two-electron reduction to hydrogen peroxide and the second wave to a further two-electron reduction to hydroxyl ions or to water. In recent years it has been claimed that, under certain conditions, the ratio of the first to the second diffusion current of oxygen at the d.m.e. can become somewhat greater than 1.00. Jordan, Ackerman, and Berger[1] reported an exaltation of 5 to 10% of the first wave when measured at −0.4 v. vs. s.c.e. in a phosphate buffer of pH 7 which was 0.1 M in potassium chloride and contained small amounts of gelatin. Cornelissen and Gierst[2] reported an unusually large exaltation of the first wave in 0.1 M tetraethyl- and 0.01 M tetrapropylammonium chloride. These cations are strongly adsorbed at the mercury–water interface and increase the ψ_d potential at the outer Helmholtz plane of the double layer. They account for the exaltation brought about by the more positive ψ_d potential by a ψ_d mechanism proposed by Kolthoff and Jordan[3] in the interpretation of the oxygen-induced electroreduction of hydrogen peroxide at a rotated platinum or gold electrode. It is shown in this paper that the exaltation of the first wave by tetraalkylammonium salts is due to a volatile impurity and that the exaltation is not observed in solutions of pure tetraalkyl salts. Griffiths and Jackman[4] claimed that in 0.1 M potassium chloride the height of the first oxygen wave is 14% (the paper states 40% but this is apparently a misprint) greater than that of the second wave and attribute this exaltation to a disproportionation reaction of hydrogen peroxide formed at the electrode. The authors do not state whether they took into account the effect of difference in drop time at potentials where the first and second diffusion currents were measured. No effort was made to eliminate stirring around the d.m.e. nor was a correction applied for the hydrogen peroxide current at potentials where the first diffusion current was measured.

In the present paper, we have made an extensive study of the polarographic reduction of oxygen under a wide variety of conditions. Admittedly, there are difficulties in finding the exact value of the first diffusion current of oxygen. In some supporting electrolytes, the first wave does not yield a plateau of constant height, the limiting current increasing slowly but continuously with increasing negative potential. This slow increase is accounted for by a contribution to the current by hydrogen peroxide, the reduction of which is highly irreversible. In this paper this contribution has been corrected for by subtracting from the total first reduction current that of hydrogen peroxide at corresponding potentials and concentrations. A further difficulty is that slight stirring during the growth of a mercury drop may occur in the absence of a surface active substance (SAS), even under conditions under which a polarogram looks entirely normal and no maximum is observed. Stirring can be completely eliminated in the presence of a proper SAS. Unfortunately, some of the common maximum suppressors also suppress the first diffusion current of oxygen.[5] In our

(1) J. Jordan, E. Ackerman, and R. L. Berger, J. Am. Chem. Soc., **78**, 2979 (1956).

(2) R. Cornelissen and L. Gierst, J. Electroanal. Chem., **3**, 219 (1962).

(3) I. M. Kolthoff and J. Jordan, J. Am. Chem. Soc., **74**, 4801 (1952).

(4) V. S. Griffiths and M. I. Jackman, Talanta, **9**, 205 (1962).

(5) See, e.g., K. H. Mancy and D. A. Okun, Anal. Chem., **32**, 108 (1960).
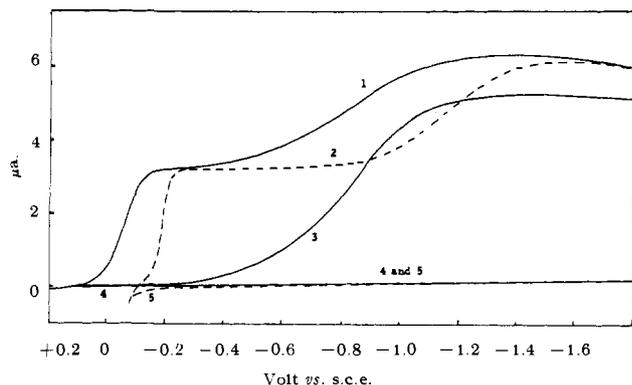
Fig. 1.—Oxygen and hydrogen peroxide waves in 0.1 M sodium perchlorate and in 0.1 M potassium hydroxide (in the absence of SAS): 1, air-saturated 0.1 M NaClO$_4$; 2, air-saturated 0.1 M KOH; 3, air-free, ca. 5 × 10^{-4} M H$_2$O$_2$ in 0.1 M NaClO$_4$; 4 and 5, air-free 0.1 M NaClO$_4$ and 0.1 M KOH, respectively.

work, we have found that polyacrylamide (PAA)[6] in small concentration is an effective suppressor of stirring, while it does not suppress the diffusion current of oxygen. In the presence of 0.005% PAA, the first and second diffusion currents of oxygen were found to be equal, provided that the first limiting current was corrected for the reduction current of hydrogen peroxide. In many instances, we have measured both the average and the maximum value of the limiting current during a drop life, the ratio of the two giving indication of the occurrence of slight stirring in the solution close to the electrode surface during the growth of a mercury drop. Whenever desirable, current–time curves have been determined. Knowing the exact values of the diffusion currents of oxygen, we have calculated the diffusion coefficient of oxygen in solutions of a few supporting electrolytes by employing the most probable relation between diffusion current and coefficient.

Apparatus and Reagents

(A) **Apparatus. Measurement of** i_{max}, **the Current at the End of a Droplife.**—This current was measured using a Leeds and Northrup Electrochemograph, Type E, without damping. This instrument records i_{max}, the value of which agrees within experimental accuracy with that obtained with oscilloscopic equipment of high-frequency response.[7,8]

Measurement of i_{av}, the average current during a drop life: This was measured using a manual polarograph.[9] Calibration of the manual polarograph against the Electrochemograph was made.

Measurement of the Current–Time Curve during a Drop Life.—The current–time curve was recorded with a Sanborn system in terms of a potential drop across a standard resistance inserted in series with the cell circuit.[10] Calibration of the scale of this instrument was made against the Electrochemograph.

Electrolysis Cell and D.m.e.—A 200-ml. tall beaker without spout was used as the electrolysis cell. A gas dispersion tube was used to saturate the solution with air and also to eliminate dissolved oxygen by passing nitrogen through it. The characteristics of the d.m.e. were: electrode A: m = 1.47 mg./sec., t = 3.8 sec. at −1.6 v. in 0.1 M potassium hydroxide + 0.005% PAA solution when the height of the mercury reservoir h was equal to 60 cm.; electrode B, m = 1.92 mg./sec., t = 3.1 sec. at −1.6 v. in 0.1 M potassium hydroxide + 0.005%-PAA solution when h = 85 cm. The potential was measured against the s.c.e. All measurements were performed at 25 ± 0.1°.

(6) I. M. Kolthoff, Y. Okinaka, and T. Fujinaga, *Anal. Chim. Acta*, **18**, 295 (1958).

(7) Leeds and Northrup Co. Catalog EM9-90(1) (1950).

(8) H. A. McKenzie and M. C. Taylor, *Australian J. Chem.*, **11**, 260 (1958).

(9) J. J. Lingane. *Anal. Chem.*, **21**, 47 (1949).

(10) I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, **80**, 4454 (1958).

(B) **Chemicals: Nitrogen Gas.**—Linde nitrogen was passed through water and then through the solution in the cell. **Air.**—Compressed air was used after washing through 0.1 M sodium hydroxide solution. **0.5% Thymol.**—Thymol (U.S.P. crystal, Baker product) was dissolved in 50% ethanol–water; 0.5% PAA was prepared from a product PAM 75 of American Cyanamid Co. **Tetramethylammonium chloride** was an Eastman Organic Chemicals product. **Tetraethylammonium chloride:** (a) An Eastman product was recrystallized from ethanol. (b) Solutions 0.1 M in the chloride were prepared by neutralizing the hydroxide with hydrochloric acid using a glass electrode to detect the end point. Two products of the hydroxide were used. One was a polarographic grade commercial product from Southeastern Analytical Chemicals. The other was a solution prepared by shaking recrystallized tetraethylammonium bromide with silver oxide.

Other reagents were of analytical grade and used without further purification.

Determination of Oxygen Concentration.—The oxygen concentration in air-saturated solution was determined by Winkler's method.[11] At 745 mm. barometric pressure and 25°, the concentration of oxygen was found to be 2.47$_5$ × 10^{-4} M in 0.1 M sodium perchlorate and 0.1 M potassium hydroxide.

Experimental Results

(A) **Oxygen Waves in 0.1 M Sodium Perchlorate and in 0.1 M Potassium Hydroxide. Absence of SAS.** —From Fig. 1 it is seen that in 0.1 M hydroxide the first oxygen wave has a diffusion current plateau of constant height between −0.3 and −0.6 v., whereas in 0.1 M perchlorate the first limiting current increases slightly, but continuously, between −0.2 and −0.5 v. In perchlorate medium the wave of 5 × 10^{-4} M hydrogen peroxide is very much drawn out (curve 3), while in 0.1 M hydroxide this current is equal to the residual current up to −0.6 v. No correction for the hydrogen peroxide current needs to be made for the first limiting current in 0.1 M hydroxide when this current is measured at potentials less negative than −0.6 v. Under our experimental conditions the concentration of oxygen was 2.5 × 10^{-4} M corresponding to the formation of 5 × 10^{-4} M hydroxyl ions at the electrode surface on the first diffusion plateau of oxygen in 0.1 M sodium perchlorate. The reduction current of 5 × 10^{-4} M hydrogen peroxide in 0.1 M perchlorate and 5 × 10^{-4} M hydroxide measured at potentials up to −0.6 v. was found to be almost the same but slightly smaller than that in the absence of hydroxide. The limiting current of oxygen at −0.3 v. in air-saturated solution of 0.1 M sodium perchlorate was corrected for the current of 2.5 × 10^{-4} M hydrogen peroxide in the same supporting electrolyte which was also 5 × 10^{-4} M in sodium hydroxide. In 0.1 M potassium hydroxide the observed current at −0.4 v. was corrected for the residual current of the supporting electrolyte. In both supporting electrolytes the second (total) diffusion current was corrected for the residual current. Results are presented in Tables I and II. The notations $(i_1)_{max}$ and $(i_t)_{max}$ refer to the first and total diffusion current of oxygen (found after application of the proper corrections) at the end of the drop life, while $(i_1)_{av}$ and $(i_1)_{av}$ denote the average values during the droplife. The drop time t is given in seconds. Column 4 in Tables I and II gives the ratio of the (corrected) heights of the first and second waves, i_2 being equal to $i_t - i_1^*$ and i_1^* being the value of the first diffusion current at the potential where i_t was measured ($t^{1/6}$ effect). This correction was calculated

(11) "Standard Method for the Examination of Water, Sewage, and Industrial Waters," Am. Public Health Assoc., Inc., New York, N. Y., 1955, p. 252.

TABLE I

i_1*/i_2 AND i_{av}/i_{max} OF OXYGEN WAVES IN 0.1 M NaClO₄.

ELECTRODE A, $i^* = i_1(t_2/t_1)^{1/6}$

h, cm.		i_1 (μa.), −0.3 v.	i_t (μa.), −1.4 v.	i_1*/i_2	i_{av}/i_{max} (exptl.) −0.3 v.	−1.4 v.	i_{av}/i_{max} (calcd.) −0.3 v.	−1.4 v.
		(a)	In the absence of SAS					
	i_{max}	3.22	6.16	1.02	0.800	0.775		
60	i_{av}	2.58	4.78	1.09				
	t	5.73	4.59					
		(b)	In the presence of 10⁻⁴% thymol					
	i_{max}	3.21	6.23	0.99	0.795	0.759		
60	i_{av}	2.60	4.73	1.13				
	t	5.71	4.60					
		(c)	In the presence of 0.005% PAA					
	i_{max}	2.65	5.09	1.00	0.807	0.795	0.796	0.798
40	i_{av}	2.14	4.04	1.04				
	t	8.51	6.76					
	i_{max}	2.92	5.62	1.00	0.811	0.801	0.801	0.803
50	i_{av}	2.37	4.50	1.02				
	t	6.73	5.33					
	i_{max}	3.18	6.07	1.02	0.805	0.805	0.806	0.807
60	i_{av}	2.56	4.89	1.02				
	t	5.58	4.46					
	i_{max}	3.62	6.90	1.02	0.798	0.802	0.812	0.813
80	i_{av}	2.89	5.54	1.01				
	t	4.11	3.25					
	i_{max}	3.97	7.56	1.01	0.806	0.816	0.816	0.817
100	i_{av}	3.20	6.18	0.99				
	t	3.29	2.53					

TABLE II

i_1*/i_2 AND i_{av}/i_{max} OF THE OXYGEN WAVES IN 0.1 M KOH.

ELECTRODE 1, $i^* = i_1(t_2/t_1)^{1/6}$

h, cm.		i_1 (μa.), −0.4 v.	i_t (μa.), −1.6 v.	i_1*/i_2	i_{av}/i_{max} (exptl.) −0.4 v.	−1.6 v.	i_{av}/i_{max} (calcd.) −0.4 v.	−1.6 v.
		(a)	In the absence of SAS					
	i_{max}	3.19	6.07	0.985	0.815	0.773		
60	i_{av}	2.60	4.69	1.10				
	t	5.77	4.10					
		(b)	In the presence of 10⁻⁴% thymol					
	i_{max}	3.15	5.94	1.10	0.805	0.769		
60	i_{av}	2.55	4.56	1.12				
	t	5.80	4.06					
		(c)	In the presence of 0.005% PAA					
	i_{max}	2.65	4.93	1.02	0.785	0.795	0.795	0.797
40	i_{av}	2.08	3.92	0.99				
	t	8.43	5.82					
	i_{max}	2.95	5.46	1.04	0.800	0.802	0.799	0.801
50	i_{av}	2.36	4.38	1.03				
	t	6.72	4.67					
	i_{max}	3.20	5.92	1.03	0.810	0.807	0.805	0.806
60	i_{av}	2.59	4.78	1.03				
	t	5.52	3.80					
	i_{max}	3.65	6.67	1.05	0.804	0.821	0.811	0.812
80	i_{av}	2.93	5.48	1.01				
	t	4.13	2.87					
	i_{max}	4.01	7.36	1.04	0.808	0.822	0.816	0.816
100	i_{av}	3.24	6.06	1.01				
	t	3.28	2.25					

using the original Ilkovic equation. In both supporting electrolytes in the absence of SAS, values of i_1*/i_2 calculated from i_{max} are practically equal to 1, but those found from i_{av} are equal to 1.1, indicating an apparent exaltation of the first wave (v.i.). The tables also list values of i_{av}/i_{max}, which in the absence of SAS are 4% larger at −0.3 (or −0.4) v. than at −1.4 (or −1.6) v.
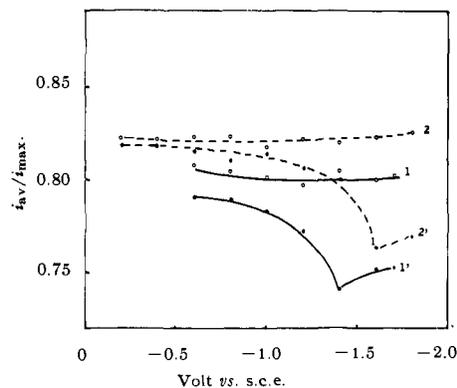
Fig. 2.—i_{av}/i_{max} vs. potential for 1 × 10⁻³ M thallium(I) and 1 × 10⁻³ M copper(II) waves in 0.1 M sodium perchlorate: 1, thallium + 0.005% PAA; 1', thallium + 10⁻⁴% thymol; 2, copper + 0.005% PAA; and 2', copper + 0.005% Na n-dodecyl sulfate.

Presence of Thymol.—The presence of 10⁻⁴% thymol in the solutions did not change the waves or any of the values reported above in the absence of SAS (Tables I and II).

Presence of 0.005% PAA.—The effect of changing the height of the mercury reservoir h was measured in the presence of 0.005% PAA (Tables I and II). In both supporting electrolytes, the average values of i_1*/i_2 are equal to 1.02 both for i_{av} and i_{max}. The values of i_{av}/i_{max} are now the same for both the first and the total wave, and equal to 0.80.

Values of i_{av}/i_{max} have also been measured for thallium(I) and copper(II) in 0.1 M sodium perchlorate and are plotted in Fig. 2. In the presence of 0.005% PAA, i_{av}/i_{max} is 0.80 for thallium and 0.82 for copper at potentials over the entire diffusion current plateau range. With thymol or sodium n-dodecyl sulfate, i_{av}/i_{max} decreases by several per cent at potentials of desorption of these surfactants.

In Fig. 3 are plotted log i–log t curves for the reduction of oxygen in 0.1 M potassium hydroxide. Currents were corrected for the residual current. In the
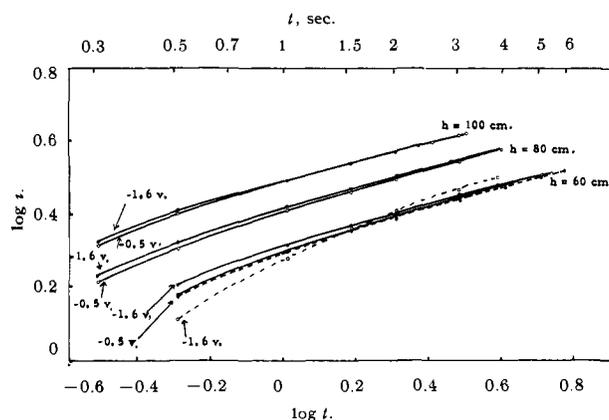
Fig. 3.—log i–log t curves during the drop life in air-saturated 0.1 M potassium hydroxide: solid lines, 0.005% PAA; dotted lines, 10⁻⁴% thymol; log i–log t at −0.5 v. and log $(i/2)$–log t at −1.6 v.

presence of 0.005% PAA, which is adsorbed over the entire potential range covered, log i–log t curves at −0.5 v. practically overlap with log $i/2$–log t curves at −1.6 v., even though the drop times are quite different. The small discrepancy at the beginning of the droplife is probably caused by the difference in the depletion effect

TABLE III

DIFFUSION COEFFICIENT OF OXYGEN IN AIR-SATURATED 0.1 M NaClO$_4$ AND 0.1 M KOH

C_{O_2} was 0.2475 mM at 25° and mercury pressure 745 mm.; electrode A was used

Solution	$(i_d)_{max}$, μa.	$(i_d)_{av}$, μa.	t, sec.	m, mg./sec.	E, v. vs. s.c.e.	h, cm.	$-D$, cm.²/sec. $\times$ 10⁵ Ilkovic equation	Modified
0.1 M KOH	7.36	..	2.25	2.45	−1.6	100	2.55	1.96
+ 0.005% PAA	4.01	..	3.28	2.45	−0.4	100	2.67	2.01
	..	6.06	2.25	2.45	−1.6	100	2.35	1.97
	..	3.24	3.28	2.45	−0.4	100	2.39	1.97
	5.92	..	3.80	1.47	−1.6	60	2.73	1.95
	3.20	..	5.52	1.47	−0.4	60	2.83	1.97
	..	4.78	3.80	1.47	−1.6	60	2.43	1.94
	..	2.59	5.52	1.47	−0.4	60	2.51	1.98
0.1 M NaClO$_4$	7.56	..	2.57	2.45	−1.4	100	2.57	1.95
+ 0.005% PAA	..	6.18	2.57	2.45	−1.4	100	2.34	1.94
	6.07	..	4.46	1.47	−1.4	60	2.70	1.92
	..	4.89	4.46	1.47	−1.4	60	2.40	1.90

at the two different drop times. The log i–log t curve at −0.5 v. in the presence of 10^{-4}% thymol practically overlaps with that in the presence of 0.005% PAA. However, a similar plot for half of the total diffusion current at −1.6 v. does neither overlap with that for the current at −0.5 v. nor with that for half of the total diffusion current in the presence of 0.005% PAA. The reason is that the thymol is desorbed at about −1.0 v.

(B) Oxygen Waves in 0.1 M Tetramethyl- and in 0.1 M Tetraethylammonium Chloride as Supporting Electrolytes.—Current potential curves of oxygen and hydrogen peroxide in these supporting electrolytes in the presence of 0.005% PAA are presented in Fig. 4.
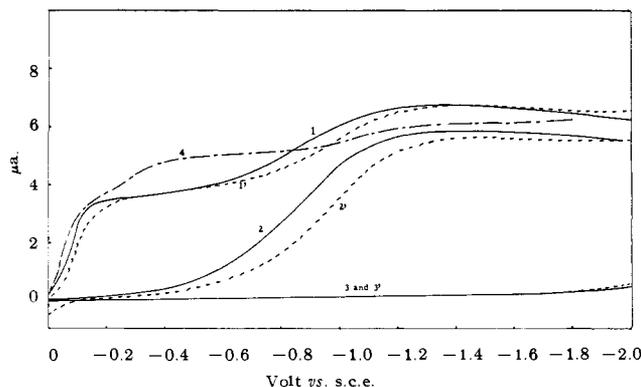
Fig. 4.—O$_2$ (air-saturated) and H$_2$O$_2$ (5 × 10^{-4} M) in 0.1 M (CH$_3$)$_4$NCl and 0.1 M (C$_2$H$_5$)$_4$NCl in the presence of 0.005% PAA (electrode B was used): 1, O$_2$ in 0.1 M (CH$_3$)$_4$NCl; 2, H$_2$O$_2$ in 0.1 M (CH$_3$)$_4$NCl; 3, residual current in 0.1 M (CH$_3$)$_4$NCl; 1', 2', and 3'. in pure 0.1 M (C$_2$H$_5$)$_4$NCl; 4, O$_2$ in impure 0.1 M (C$_2$H$_5$)$_4$NCl, pH 6, not completely air-saturated, without PAA.

The curves are very similar to those in 0.1 M sodium perchlorate. In this experiment, electrode B was used instead of electrode A. In the absence of PAA, i_1^*/i_2 in (CH$_3$)$_4$NCl was 0.95 for i_{max} and 1.10 for i_{av}, respectively; in (C$_2$H$_5$)$_4$NCl these figures were 1.01 and 1.08. Values of i_{av}/i_{max} at −0.3 and −1.3 v., respectively, were 0.813 and 0.753 for tetramethylammonium salt. For tetraethylammonium chloride values of i_{av}/i_{max} were 0.785 at −0.3 v. and 0.757 at −1.5 v. In the presence of 0.005% PAA the average value of i_1^*/i_2 was 1.01 and of i_{av}/i_{max} 0.785 in both supporting electrolytes. These ratios in the presence of PAA are practically equal to those found in 0.1 M sodium perchlorate plus 0.005% PAA (Table I) and 0.1 M potassium hydroxide plus 0.005% PAA (Table II).

Curve 4 is the current–potential curve in air containing (but unsaturated) solution of 0.1 M tetraethylammonium chloride prepared by neutralization of the hydroxide to pH 6. There is an apparent large exaltation of the first oxygen wave, the total wave height at −1.6 v. being the same as that observed in pure salt. The apparent exaltation is due to a volatile impurity. This was shown in two ways. After passing nitrogen through the solution for 20 min. and saturating again with air no exaltation was observed and the current potential curve overlapped with that observed in pure tetraethylammonium chloride (curve 1' in Fig. 4). The impurity removed on passing nitrogen was collected at liquid nitrogen temperature in a trap and added to an air-saturated solution of 0.1 M pure tetraethylammonium chloride. Exaltation was observed again like in curve 4 of Fig. 4. A further discussion of the effect of the impurity formed in solutions of tetraethylammonium hydroxide and of other substances which give rise to an apparent exaltation is beyond the scope of this paper and will be presented in a subsequent paper.

Discussion

The diffusion coefficient D of oxygen was calculated from the data presented in Tables I and II. The general form of the modified Ilkovic equation is

$$i_d = AnD^{1/2}Cm^{2/3}t^{1/6}(1 + BD^{1/2}m^{-1/3}t^{1/6} + CDm^{-2/3}t^{1/3})$$

where $A = 708$ for i_{max} and 607 for i_{av}.

Various values of B have been proposed in the literature.[12-18] After a critical study of these papers it appeared reasonable to use the value proposed by Koutecky for i_{max},[16] neglecting the C term, which is permissible for our purposes, as it is very small.

$$i_{max} = 708nD^{1/2}Cm^{2/3}t^{1/6}(1 + 39D^{1/2}m^{-1/3}t^{1/6}) \quad (1)$$

The diffusion coefficient of oxygen was calculated from i_{max}. Values of the diffusion coefficient of oxygen using eq. 1 and also the original Ilkovic equation are listed in Table III. The average values of D at 25° from eq. 1 are 1.97 (±0.02) × 10^{-5} cm.²/sec. in 0.1 M potassium hydroxide and 1.94 (±0.02) × 10^{-5} cm.²/sec. in 0.1 M sodium perchlorate.

(12) J. J. Lingane and B. A. Loveridge, *J. Am. Chem. Soc.*, **72**, 438 (1950).
(13) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).
(14) T. Kambara and I. Tachi, *Bull. Chem. Soc. Japan*, **25**, 284 (1952).
(15) J. Koutecky, *Czechoslov. J. Phys.*, **2**, 50 (1953).
(16) H. Matsuda, *Bull. Chem. Soc. Japan*, **26**, 342 (1953).
(17) W. Hans, W. Henne, and E. Meurer, *Z. Elektrochem.*, **58**, 836 (1954).
(18) D. J. Macero and C. L. Rulfs, *J. Am. Chem. Soc.*, **81**, 2944 (1959).

Using the above values of the diffusion coefficients it is now possible to calculate from the experimental average current i_{av} the value of B in the modified Ilkovic equation. For electrode A we find

$$i_{av} = 607nD^{1/2}Cm^{2/3}t^{1/6}(1 + 25D^{1/2}m^{-1/3}t^{1/6}) \quad (2)$$

There is no universal value for B in the expression for i_{av}, because it is affected by the magnitude of the depletion effect which in turn depends upon the characteristics of the capillary and also by the diffusion coefficient of the electroactive species. The variation of B with m and t of the capillary is small for a given electrode. However, for the purposes of calculating diffusion coefficients, it is recommended that i_{max} be measured and eq. 1 be used.

Values of i_{av}/i_{max} calculated using eq. 1 and 2 and the reported value of the diffusion coefficient of oxygen (Table III) are presented in the last two columns of Tables I and II. In the presence of 0.005% PAA these values are in excellent agreement with the experimental values. For thallium(I) and copper(II) in the presence of 0.005% PAA the calculated values of i_{av}/i_{max} are 0.80_6 and 0.82_5, respectively, as compared to the experimental values of 0.80_3 and 0.82_2.

Values of i_{av}/i_{max} for the first oxygen diffusion current in 0.1 M sodium perchlorate or potassium hydroxide in the absence of SAS or the presence of 10^{-4}% thymol are the same as in the presence of 0.005% PAA (Tables I and II). However, at the potentials at which the total diffusion current is measured, i_{av}/i_{max} is several percent smaller in the absence of SAS or in the presence of 10^{-4}% thymol (thymol is desorbed at this potential) than in the presence of 0.005% PAA. This indicates that at these negative potentials there is a slight stirring (due to the occurrence of a slight maximum of the second kind) of the liquid around the electrode in the absence of PAA. Values of $(i_t)_{max}$ decrease slightly in the presence of 0.005% PAA, but those of $(i_t)_{av}$ increase slightly (Tables I and II). It has been reported that a slight maximum of the second kind enhances the depletion effect.[17,19] The dotted curve at -1.6 v. in Fig. 3 clearly illustrates this enhanced depletion of electroactive substance around the electrode in the absence of PAA during the early stage of the drop life. (Owing to the slight maximum of the second kind, the current at the end of the drop life is slightly larger in the absence of PAA than in its presence.) Because of this enhanced deple-

(19) M. von Stackelberg, *Rev. Polarography*, **5**, 120, 133 (1957).

tion, $(i_t)_{av}$ at -1.6 v. in the absence of PAA is smaller than that in the presence of 0.005% PAA, even though the opposite is true for $(i_t)_{max}$.

In the calculation of the value of the first diffusion current i_1^* at the potential where the total diffusion current i_t was measured it was assumed that the original Ilkovic equation instead of the modified equation is valid. The error thus made is small and can be neglected for most practical purposes. Actually the first diffusion current $(i_1)_{t_2}$ at the drop time t_2, where i_t is measured, is equal to

$$(i_1)_{t_2} = (i_1)t_1 \left(\frac{t_2}{t_1}\right)^{1/6} \frac{1 + BD^{1/2}m^{-1/3}t_2^{1/6}}{1 + BD^{1/3}m^{-1/3}t_1^{1/6}}$$

$$= i_1^* \frac{1 + BD^{1/2}m^{-1/3}t_2^{1/6}}{1 + BD^{1/2}m^{-1/3}t_1^{1/6}}$$

in which t_1 is the drop time at which $(i_1)_{t_1}$ is measured. Therefore, i_2 is not equal to $i_t - i_1^*$, but

$$i_2 = i_t - (i_1)_{t_2}$$

Applying eq. 1 and 2, taking into account that the first wave involves two and the total wave four electrons, eq. 3 is obtained.

$$\frac{i_1^*}{i_2} = \frac{1 + BD^{1/2}m^{-1/3}t_1^{1/6}}{1 + BD^{1/3}m^{-1/3}(2t_2^{1/6} - t_1^{1/6})} \quad (3)$$

For i_{max} ($B = 39$) and for i_{av} ($B = 25$), a ratio of 1.02 is calculated. The average of all the values reported in Tables I and II in the presence of 0.005% PAA is 1.02 $\pm$ 0.01.

From the data presented in this paper it may be stated definitely that there is no exaltation of the first oxygen wave provided that stirring of the liquid close to the electrode is eliminated by addition of 0.005% PAA, and when correction is made for the contribution to the current by hydrogen peroxide formed in the reduction of oxygen. On the other hand, in the absence of PAA, the average value of i_1^*/i_2 (Tables I and II) for the average current is 1.11 $\pm$ 0.02, indicating an apparent exaltation of the first wave. This high value is accounted for by the fact that, as a result of slight stirring around the electrode in the absence of PAA, $(i_t)_{av}$ is smaller than when 0.005% PAA is present.