OXIDATION OF HYDROGEN PEROXIDE
AT THE DROPPING MERCURY ELECTRODE

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Reduction of oxygen and oxidation of hydrogen peroxide at the dropping mercury electrode are electrochemical processes strongly influenced both by the pH value and the anions in solution. With decreasing pH, both processes become irreversible, especially in the presence of anions with a negative φ_2 potential of the diffusion part of the double layer. In the case of irreversible oxygen reduction, the concept that the rate-controlling step of the electrode process is the acceptance of the first electron with the formation of the superoxide anion, O_2^-, was substantiated. Oxidation of hydrogen peroxide becomes irreversible at a lower pH value than the reduction of oxygen. The slowest, *i.e.* rate-controlling step of the electrode process in borate buffers at pH 9—10 is the transfer of the second electron, *i.e.* oxidation of superoxide to oxygen.

The course of electrochemical processes connected with the $O_2/H_2O_2/H_2O$ system is strongly dependent on the properties of both the electrode and electrolyte. Important factors are the electrode material, its internal (with porous electrodes) and surface structure, and the presence of even small amounts of catalytically active substances on the electrode surface, in the electrolyte, or in the electrode[1−4]. The resulting equilibrium potential of the O_2/H_2O redox system is influenced mainly by the formation of the intermediate product, H_2O_2. Two-stage reduction of oxygen *via* relatively stable intermediate product, H_2O_2, can be observed on mercury[5], gold[1,2], and carbon[1−4] electrodes if their activity is not enhanced by adding a suitable catalyst into the solution, into the electrode, or on its surface. The catalysts enhance the first wave of oxygen reduction to hydrogen peroxide on the polarographic or voltammetric curves, or they cause a shift of a part of the peroxide reduction wave to more positive potentials at the expense of the original peroxide reduction wave. The activity of the catalysts may be related either to the catalysis of the decomposition of hydrogen peroxide formed at the electrode or to promoting its reduction through the formation of an adduct of the catalyst with oxygen or peroxide.

The oxidation of hydrogen peroxide at noncatalysed carbon electrodes proceeds at much more positive potentials than the reduction of oxygen[3,4]. A similar situation exists in the case of a mercury electrode in acidic solutions, whereas at pH > 10 the O_2/H_2O_2 system is reversible, giving rise to the formation of a reversible anodic-cathodic wave[6].

The reduction of oxygen proceeds at platinum[7,8] and silver[9] electrodes, as far as they are not inhibited by adsorbed surface-active substances, in a single four-electron wave, observable on the voltammetric curves. Even in these cases, the formation of H_2O_2 as intermediate product was proved by experiments with silver[3] or platinum[7] disk electrodes with a ring.

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During a study of the effect of the electrode double layer on the polarographic reduction of oxygen at the dropping mercury electrode[10], the standard rate constant $\overline{k}^0$ of the process was found to be dependent on pH and the potential φ_2 of the outer Helmholtz plane. The dependence of $\overline{k}^0$ on pH was described also recently[11].

The present work deals mainly with the oxidation of hydrogen peroxide at the dropping mercury electrode and its comparison with the reduction of oxygen.

EXPERIMENTAL

Polarographic curves were recorded on a Radelkis OH 102 type polarograph (Hungary) with the use of a Kalousek cell with a separated Hg/HgO or calomel reference electrode. All potential values given in the text below are referred to S.H.E. The potential of the Hg/HgO electrode was measured and corrected for the liquid junction potential against S.C.E. (0·241 V vs S.H.E). The drop time was adjusted by a drop time controller manufactured in this Institute.

The chemicals used were of reagent grade (Lachema, Brno), the solutions were prepared from redistilled water. The ionic strength was mostly kept constant at $\mu = 0\cdot2$ by the addition of NaNO$_3$. The pH value of buffered solutions was measured on a Vibron 39A type pH meter with a glass electrode (Electronic Instruments, England). Oxygen was removed from the solutions by bubbling argon of 99·99% purity, if necessary.

RESULTS

The limiting current due to oxidation of hydrogen peroxide could not be measured at pH < 7·0 and its measurement was not accurate even in the pH range 7·0−8·3. Borate buffers and NaOH solutions served as base electrolytes to cover a wide range of pH values.

Reversible Redox Reaction O$_2$ $\rightleftharpoons$ H$_2$O$_2$

Similarly to the case of oxygen reduction[6,10], the character of the electrode process depends on pH also in the case of peroxide oxidation. The half-wave potential and the slope of the anodic wave correspond to a reversible process at pH > 10. Theoretical values of $E_{1/2}$ for the reversible reaction O$_2$ $\rightleftharpoons$ H$_2$O$_2$ are compared with the measured values $(E_{1/2}^{cat})$ for oxygen reduction and those for oxidation of peroxide $(E_{1/2}^{an})$ in Table I. The numbers of electrons, t_{cat} and z_{an}, participating in the electrode reaction on the assumption of reversibility were determined from the dependences of $\log\left[i/(i_d - i)\right]$ (denoted as L_c) and $\log\left[(I_d - i)/i\right]$ (L_a) on E. Here, I_d and i_d denote the limiting diffusion currents of peroxide oxidation and oxygen reduction, respectively, and i is the current at the potential E. The values for the oxygen reduction are also indicated at lower pH values, where they do not quite correspond to a reversible reduction process, for comparison with the different character of peroxide oxidation. Accordingly, the reduction of oxygen can under the given conditions be considered reversible at pH approaching 12, whereas the oxidation of peroxide

acquires a reversible character at pH as low as 10·5. Hence, the values of z_{cat} denoted by superscript a do not correspond to the number of exchanged electrons.

The anodic wave for oxidation of H_2O_2 in alkaline medium coincides with the cathodic wave for oxygen reduction to form a single anodic-cathodic wave with the value of $E_{1/2}$ equal to the theoretical. The logarithmic analyses of the cathodic wave for oxygen $(L_c = f(E))$ and anodic wave for peroxide $(L_a = f(E))$ in alkaline medium yield identical straight lines.

Quasireversible and Irreversible Reduction of Oxygen

In borate buffers of pH < 11·0, the reduction of oxygen was not found to be reversible. The rate constants of the electrode process (Table II) at pH $9·61 - 10·60$ were calculated from the measured data according to the method[12] for quasireversible processes as

$$k^0 = \frac{i'}{i_d - 2i'} \frac{\sqrt{(D_{red}^\alpha D_{ox}^{1-\alpha})}}{0·886 t_1^{1/2}},$$

where D_{red} and D_{ox} denote diffusion coefficients of the reduced and oxidized forms, t_1 denotes drop time, α transfer coefficient, and i' current corresponding to the reversible half-wave potential $E_{1/2}^r$ (Fig. 1). The values of the constants are comparable with those in ref.[10]. For pH < 9·6, the rate constants were calculated from the equation[5]

TABLE I

Electrochemical data for reduction of oxygen and oxidation of hydrogen peroxide at pH 10·6 to 13·0. Potentials against s.h.e.; $\mu = 0·2$, borate buffer pH $10·60 - 12·15$

pH	$E_{1/2}^{teor}$ mV	Reduction of O_2		Oxidation of H_2O_2	
		$E_{1/2}^{cat}$ mV	z_{cat}	$E_{1/2}^{an}$ mV	z_{an}
10·60	+143	+121	0·74[a]	+141	1·96
10·97	+123	+101	1·3[a]	+121	2·0
11·90	+ 80	+ 75	1·88	+ 78	2·0
12·15	+ 70	+ 67	1·96	+ 69	1·98
0·01M-NaOH	+ 76	+ 78	1·97	+ 75	1·98
0·1M-NaOH	+ 42	+ 43	1·99	+ 42	2·0

[a] Calculated from the slope of the tangent to the logarithmic dependence at negative potentials, where $i \approx i_d$ according to the method[12] for quasireversible processes.

$$\log \bar{k}^0 = \frac{\alpha z}{0 \cdot 059} \left(E_{1/2} - E_{1/2}^{\text{theor}} \right) - \log \left(0 \cdot 886 t_1 / D_{\text{ox}} \right).$$

The factor αz was in the case of pH > 8, where the logarithmic analysis did not give a straight line, calculated from the slope of the tangent of the logarithmic dependence at negative potentials[12]. An ideal straight line was obtained in logarithmic coordinates for irreversible reduction of oxygen in acetate buffer of pH 4·8.

The values of $\bar{k}^0$ for pH 9·2 and lower could not therefore be determined by the method valid for quasireversible reactions. The values calculated by this method at pH 9·2 were much higher than at pH $\geqq 9\cdot6$ as a consequence of inaccurate determination of i' on the curve in logarithmic coordinates.

The measured half-wave potentials for oxygen reduction are practically independent of pH up to pH $= 10$, the differences being in the range of experimental errors. The dependence on pH corresponding to the reversible behaviour is observed only at pH > 11.

The dependence of $\bar{k}^0$ on pH (Fig. 2) is a straight line with minor deviations at pH $7\cdot7 - 9\cdot2$, where the method for quasireversible processes[12] could not be used. The slope of the straight line $d\bar{k}^0/d$ pH $= 0\cdot057$.

Irreversible Oxidation of Hydrogen Peroxide in Borate Buffer

As stated above, oxidation of hydrogen peroxide in borate buffer solutions preserves its reversible character down to lower pH (almost 10) than reduction of oxygen

TABLE II

Electrochemical data for irreversible reduction of oxygen. Potentials against s.h.e.; $\mu = 0\cdot2$; pH $7\cdot71 - 10\cdot60$ in borate buffers, 4·8 in acetate buffer

pH	$E_{1/2}^{\text{teor}}$ mV	$E_{1/2}$ mV	$\bar{k}^0 \cdot 10^3$ cm s^{-1}	αz
4·80	485	194	0·013	0·52
7·71	313	158	0·32	0·48
8·23	282	161	0·48	0·51
8·42	271	166	0·69	0·50
8·80	249	166	1·3	0·46
9·20	225	171	2·0	0·48
9·61	201	167	4·1	0·52
9·81	189	163	4·8	0·58
9·90	184	159	5·8	0·58
10·01	176	152	7·1	0·61
10·60	143	121	15·0	0·74

(Tables I—III). In contrast to reduction of oxygen, we did not obtain a nonlinear logarithmic analysis of the wave, hence it is not possible to calculate the electrode reaction parameters by the method[11] derived for quasireversible processes. A noteworthy feature is the change of the product ωz with pH, where ω is the generalized charge transfer coefficient and z is the number of exchanged electrons in the electrode reaction. This product changes from a value corresponding to almost reversible two-electron oxidation $(\omega = 1, z = 2)$ to about 1. The coefficient ω was introduced in order to follow the gradual change of the character of the electrode reaction with decreasing pH from a reversible to an irreversible one. The rate constant at pH about 10 cannot be determined from the equation for irreversible processes since the overpotential is too low. The logarithmic analysis of the anodic wave in the given pH range yields a straight line, hence the method for quasireversible processes could not be used either. For the pH range 7·71 — 8·42, where the overpotential of the anodic oxidation of peroxide was higher than 0·05 V, the rate constant values were calculated to be in the range $3\cdot0 - 6\cdot0 \cdot 10^{-4}$ cm s^{-1}.
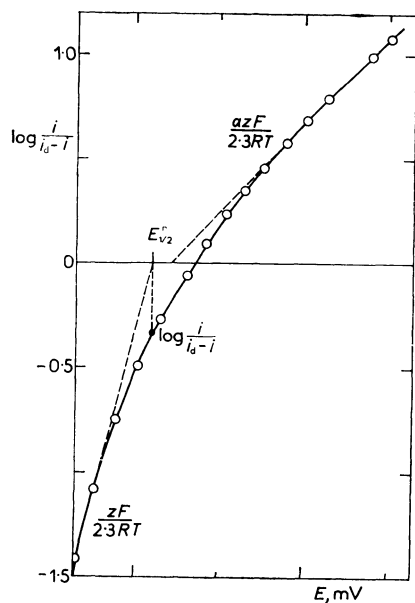

FIG. 1

Logarithmic analysis of the quasireversible cathodic wave of oxygen in borate buffer; pH 9·81, $\mu = 0\cdot2$ adjusted by addition of NaNO$_3$. The value of i' is calculated from log $[i'/(i_d - i')]$
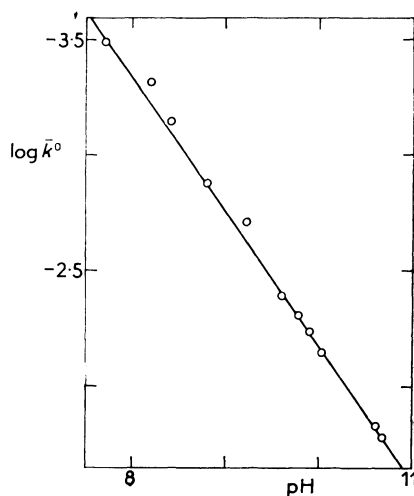
FIG. 2

Dependence of log $\bar{k}^0$ (for oxygen reduction) on pH in borate buffers; $\mu = 0\cdot2$ adjusted by addition of NaNO$_3$

Influence of the Electrode Double Layer on the Reduction
of Oxygen and Oxidation of Hydrogen Peroxide

The electrochemical parameters of the studied reactions are in borate buffer solutions strongly dependent on the concentration of tetraborate anions (Table IV). They were calculated as for completely irreversible processes and without correction for the φ_2 potential. With increasing borate concentration, the half-wave potential for oxygen reduction is shifted to higher negative values, and for peroxide oxidation to higher positive values. Hence, the overpotential increases in both cases. At the

TABLE III

Electrochemical data for oxidation of hydrogen peroxide in borate buffers. Potentials against s.h.e.; $\mu = 0.2$ adjusted by addition of $NaNO_3$; ω coefficient characterizing the charge transfer (see Discussion)

pH	$E_{1/2}^{teor}$ mV	$E_{1/2}$ mV	ωz
7·71	313	384	1·02
8·23	282	340	1·04
8·42	271	324	1·09
8·80	249	288	1·23
9·20	225	252	1·40
9·61	201	220	1·44
9·90	184	198	1·52
10·01	176	185	1·91

TABLE IV

Influence of tetraborate anions on electrochemical parameters for oxygen reduction and peroxide oxidation (ionic strength nonadjusted)

$[Na_2B_4O_7]$ mol/l	μ	Reduction of O_2			Oxidation of H_2O_2	
		$E_{1/2}^{cat}$ mV	αz	$\overline{k}^0 . 10^3$ cm s^{-1}	$E_{1/2}^{an}$ mV	ωz
0·05	0·15	185	0·60	2·1	231	1·48
0·10	0·30	161	0·56	1·5	250	1·40
0·15	0·45	154	0·55	1·2	266	1·26
0·20	0·60	148	0·55	1·0	265	1·23

same time, the charge transfer coefficient found from logarithmic analysis decreases. The influence of borate anions on the anodic-cathodic waves of oxygen in the presence of peroxide is illustrated in Fig. 3. A comparison of the waves in $0.05M$-$Na_2B_4O_7$ in the absence of nitrate ions $(\mu = 0.15)$ and in their presence $(\mu = 0.2)$ shows that nitrate ions enhance the irreversibility of both processes. The dependence of the corresponding electrochemical parameters on the ionic strength adjusted by additions of nitrate to a solution of $0.05M$-$Na_2B_4O_7$ (pH 9.20) is shown in Table V. It is seen from the last two tables that the overpotential of oxygen reduction is increased more by borate than by nitrate ions. The rate constant values for the reduc-

TABLE V

Dependence of electrochemical parameters for reduction of oxygen and oxidation of peroxide on ionic strength in $0.05M$-$Na_2B_4O_7$ (adjusted by addition of $NaNO_3$)

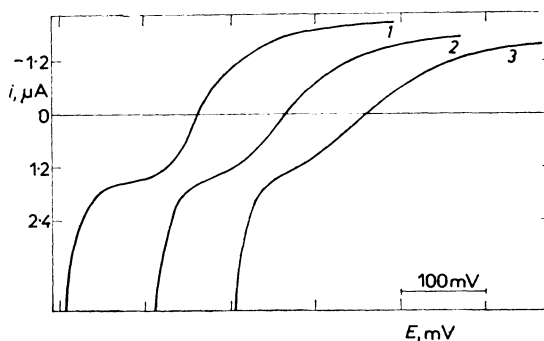| μ	Reduction of O_2			Oxidation of H_2O_2	
	$E_{1/2}^{cat}$ mV	αz	$k^0 . 10^3$ cm s^{-1}	$E_{1/2}^{an}$ mV	ωz
0.15^a	185	0.60	2.1	231	1.48
0.20	171	0.52	2.0	247	1.40
0.40	165	0.51	1.6	264	1.26
0.60	160	0.50	1.5	266	1.18

^{a} Ionic strength nonadjusted.

FIG. 3

Influence of tetraborate ions on polarographic waves of oxygen and hydrogen peroxide in the same borate buffer solution. *1* 0.05 mol/l; *2* 0.1 mol/l; *3* 0.2 mol/l $Na_2B_4O_7$. Curves recorded from + 385 mV (S.H.E.) to negative potentials and redrawn without oscillations

tion of oxygen indicated here were obtained from the equation for irreversible electrode processes. In the case of oxidation of peroxide, there is no difference between the effects of borate and nitrate.

To study the effect of anions more closely, we used an ammonia-ammonium fluoride buffer, which is effective in the same pH range as the borate buffer. Fluoride ions give rise to markedly positive φ_2 potential on the positively charged surface of the dropping electrode in the considered region of oxygen reduction and peroxide oxidation. It is seen from Table VI that the reduction of oxygen and oxidation of peroxide in the NH_3—NH_4F buffer proceed more reversibly than in the borate buffer. Therefore, the rate constant $\bar{k}$ for the reduction of oxygen can be calculated, in contrast to the borate buffer, by the method for quasireversible electrode processes. The dependence of log $\bar{k}^0$ on pH has a slope equal to 0·6.

The influence of various anions and hence the influence of the φ_2 potential on the half-wave potentials of the studied waves is shown in Table VII.

TABLE VI

Dependence of electrochemical parameters for reduction of oxygen and oxidation of peroxide on pH in NH_3–NH_4F buffer solutions; $0·1M$-Na_4F, pH adjusted by addition of NH_3

pH	$E_{1/2}^{teor}$ mV	Reduction of O_2			Oxidation of H_2O_2	
		$E_{1/2}^{cat}$ mV	αz	$\bar{k}^0 \cdot 10^2$ cm s^{-1}	$E_{1/2}^{an}$ mV	ωz
9·50	208	201	0·74	3·2	213	1·81
9·25	222	216	0·72	2·0	228	1·79
8·93	241	230	0·61	1·3	247	1·71

TABLE VII

Influence of anions on the half-wave potentials of oxygen reduction and peroxide oxidation in $0·1M$-NH_4F + $0·05M$-NH_3, pH 9·25. The difference between the $E_{1/2}$ value without and with the added anion is denoted as $\Delta E_{1/2}$

Anion added	$E_{1/2}^{cat}$ mV	$-\Delta E_{1/2}^{cat}$ mV	$E_{1/2}^{an}$ mV	$+\Delta E_{1/2}^{an}$ mV
—	216	—	228	—
$0·1N$-$NaClO_4$	196	20	242	14
$0·1N$-Na_2SO_4	194	22	244	16
$0·1N$-$NaNO_3$	172	36	247	19

DISCUSSION

In the case where the reaction $O_2 \rightleftharpoons H_2O_2$ is reversible, the measured electrochemical parameters for the two mutually opposed processes are the same. The reaction involves always two electrons, the logarithmic analyses of the waves correspond to reversible processes, and the half-wave potentials are identical. A solution containing both oxygen and hydrogen peroxide gives an anodic-cathodic wave in accord with the equation for a reversible rerox system.

However, the mentioned system is reversible only in alkaline medium at pH > 11 (Table I). At lower pH values, especially in the presence of substances inhibiting the electrode reaction, its reversibility is impaired. With decreasing pH, the reduction of oxygen begins to deviate from the reversible character in a more alkaline medium than the oxidation of peroxide; this follows not only from the deviations of the $E_{1/2}$ values from theoretical, but also from the charge transfer coefficients determined by logarithmic analyses (Tables I – III).

Similarly to the equations for the reduction of oxygen[1,4], the following scheme can be proposed for the oxidation of peroxide in alkaline media

$$HO_2^- - e^- \rightleftharpoons HO_2 \tag{A}$$

$$HO_2 - e^- \rightleftharpoons HO_2^+ \tag{B}$$

$$HO_2^+ - H^+ \rightleftharpoons O_2 \tag{C}$$

This may be modified according to the value of pH and the corresponding dissociation constants $pK_{H_2O_2} = 11.62$ and $pK_{HO_2} = 7.0$. Thus, at pH 11.6 and lower the cation $H_2O_2^+$ formed by the electrode reaction and its subsequent rapid decomposition must be taken into account, since the equilibrium will in this case be shifted towards dissociation of the cations $H_2O_2^+$ and HO_2^+.

Accordingly, the oxidation of hydrogen peroxide, similarly to the reduction of oxygen, can be described by the consecutive reactions

$$B_1 - e^- \; \underset{k_1{}^{red}}{\overset{k_1{}^{ox}}{\rightleftharpoons}} \; B_2 \tag{D}$$

$$B_2 - e^- \; \underset{k_2{}^{red}}{\overset{k_2{}^{ox}}{\rightleftharpoons}} \; B_3 \tag{E}$$

These charge-transfer reactions are, besides the standard potentials and rate constants, characterized by the charge transfer coefficients β_1 and β_2. Assuming that the rate of the overall electrode process will be determined by reaction (E), i.e. oxidation of superoxide to oxygen, we can find, in analogy to the general two-stage reduction,

similar equations[10,13] for the two-stage oxidation of hydrogen peroxide[14]. Thus, the equation of the irreversible anodic wave can be written as

$$E = E_{1/2} + \frac{RT}{(1 + \beta_2)\,F} \ln \frac{I_d - i}{i}\,, \qquad (1)$$

where $1 + \beta_2$ should correspond to the experimentally found value of ωz. This equation forms the base of the so-called logarithmic analysis.

Whereas at pH > 10 the term $1 + \beta_2$ can in logarithmic analysis[7] be replaced by $z = 2$ for reversible two-electron oxidation, at lower pH values the factor ωz must be introduced. When the latter decreases with pH to about 1·5, it is possible to set $z = 1$, $\omega = 1·5 = 1 + \beta_2$, i.e. $\beta_2 = 0·5$ corresponding to the term $1 - \alpha_1$ for the back reduction of oxygen to superoxide. For this reaction, which by its slowness causes the irreversible character of the polarographic reduction of oxygen to peroxide at pH < 11, the value of $\alpha_1 = 0·5$ has been reported[4,10] in accord with the present work (Table II). It remains not clear why the value of ωz decreases at lower pH to about 1.

Logarithmic analyses of the anodic waves of hydrogen peroxide at pH < 10 give, in contrast to the reduction of oxygen, straight lines as in the whole pH region from 7·7 to 13. The rate constants of the process could not be calculated by the method for quasireversible processes according to Koryta[12]. They were calculated from the equation for irreversible processes only in the cases where the anodic overpotential was higher than 50 mV. At pH 7·7−8·42, the calculated values were in the range $3 − 6 . 10^{-4}$ cm s^{-1}, differing not too much from the rate constants for oxygen reduction at the same conditions.

The dependences of $E_{1/2}$ on pH for the reduction of oxygen and oxidation of peroxide are different in character if these processes are irreversible. The value of $E_{1/2}$ for oxygen reduction in borate buffers at pH < 10 is practically independent of pH, evidence that protons do not participate in the rate-determining step, whereas in the case of peroxide oxidation the value of $E_{1/2}$ becomes more positive with decreasing pH. This obeys the Nernst equation for a reversible process approximately up to pH 10 with a correction for the dissociation of peroxide. At lower pH values, the dependence on pH corresponds to the influence of deprotonation of the superoxide cation on the rate-determining step.

The slope of the dependence of log $\bar{k}^0$ on pH in borate buffers is equal to 0·57, which differs only little from the value of 0·55 obtained and derived theoretically[10]. This dependence is fairly well satisfied also by the values of $\bar{k}^0$ at pH < 9·6, which are not included in ref.[10].

The electric field due to the charge of the electrode influences not only the activation energy of the electrode reaction, but also the concentrations of the reactants

at the electrode. The basic kinetic equation for the cathodic reduction can be written as[13]

$$j = j_{\varphi_2 = 0} \exp \left[(\alpha z - z_{ox}) F\varphi_2 / RT \right], \tag{2}$$

where $j_{\varphi_2 = 0}$ is the current density without correction for the φ_2 potential, *i.e.* potential difference between the outer Helmholtz plane and the bulk of the solution. Similarly, the rate constant $\bar{k}^0$ of the electrode process depends on the φ_2 potential

$$\bar{k}^0 = \bar{k}^0_{\varphi_2 = 0} \exp \left[(\alpha z - z_{ox}) F\varphi_2 / RT \right]. \tag{3}$$

Similar equations apply to the anodic reaction. They imply that if the charge of the species participating in the rate-determining step is nonpositive, the positive φ_2 potential causes a shift of $E_{1/2}$ towards the reversible value.

The results given in Tables IV and V can be elucidated by the effect of the φ_2 potential. With increasing concentration of tetraborate or nitrate ions the $E_{1/2}$ values for oxygen reduction and peroxide oxidation become more irreversible. Since these processes proceed at the given conditions on positively charged surface of the dropping mercury electrode, the mentioned effect can be attributed to specific adsorption of tetraborate and nitrate anions on the electrode in the considered potential region, which has been described elsewhere[15,16].

In the NH_4—NH_4F buffers, the reduction of oxygen and oxidation of peroxide are much more reversible than in borate buffers. This follows mainly from the relatively high positive φ_2 potential[10] in fluoride solutions at the positively charged mercury electrode.

The negative effect of perchlorate, sulphate, and nitrate anions added into the NH_3—NH_4F buffer on the reversibility of the studied processes follows from the negative values of the φ_2 potential of these anions[10,15] in the considered potential region. In addition, the specific adsorption of these anions must be taken into account.

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