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Steady-State Voltammetry for Hydroxide Ion Oxidation in Aqueous Solutions in the Absence of and with Varying Concentrations of Supporting Electrolyte

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The steady-state voltammetric behavior for the oxidation of aqueous solutions containing the strong bases sodium and barium hydroxide was studied with gold microelectrodes in the absence and in the presence of different concentrations of supporting electrolyte. A well-defined oxidation wave attributed to the oxidation of hydroxide ions to oxygen was observed in all the solutions investigated, regardless of both the nature of the base and the supporting electrolyte employed. However, in solutions with excess electrolyte, the steady-state limiting current was found to depend on the actual concentration of the supporting electrolyte, as the diffusion coefficient of the electroactive species varies with both the ionic strength and viscosity of the medium. Since the hydroxide ion is a negatively charged species, solutions with low or without supporting electrolyte yielded currents enhanced by migration contributions. Theoretical equations for the dependence of steady-state limiting currents with ionic strength were derived; theoretical and experimental data compared satisfactorily. The usefulness of the oxidation wave of hydroxide ions for analytical applications was shown by examining the dependence of steady-state limiting currents on concentration and pH. At a given ionic strength, the steady-state limiting current is proportional to the concentration of hydroxide ion over the range 0.5−5 mM. Moreover, the pH of the basic solutions can be determined by amperometry in place of potentiometry, with the use of an absolute equation.

In aqueous solutions, the cathodic and anodic potential limits at noble metals such as platinum and gold are defined by the hydrogen and oxygen evolution processes.[1] These, according to several reviews,[1−5] occur through quite complex reaction pathways. It is also well established that dilute aqueous solutions of acids show a wave for hydronium ion reduction which is separated from the background discharge to an extent that depends, for a given electrode material, on the nature of the acid.[6−16] By analogy, an oxidation wave would be expected from dilute solutions of bases, where free hydroxide ions are available to a considerable extent. Although there are many papers dealing with the anodic voltammetric behavior of noble metals in aqueous solutions of strong bases, we have not found a single article reporting a clear oxidation wave due to hydroxide ion and separated from the oxygen evolution due to the background. This, in part, can be because the anodization of noble metals involves oxide film formation.[1]

Recently,[17] during explorative measurements aimed at characterizing, under steady-state conditions, the anodic behavior of gold microelectrodes in aqueous solutions made basic with NaOH, a well-defined wave was observed at very positive potentials (∼1.3 V versus a saturated calomel electrode), just before the background discharge. In excess sodium sulfate or sodium perchlorate,

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the height of the wave was found to be proportional to the electrode radius, thus indicating a diffusive character. These findings suggested to us that the oxidation of hydroxide ions could be exploited for analytical purposes. This would parallel the hydronium ion reduction process, which can be used, under some conditions, to determine the concentration of strong and weak acids[14,16] and could expand the use of amperometry, in place of potentiometry, for monitoring the hydrogen ion level of aqueous solutions over the whole pH range. This would obviously be accomplished by exploiting the reduction of hydronium ions in acidic media, the oxidation of hydroxide ions in basic solutions, and considering that the concentration of hydrogen and hydroxide ions are related through the water dissociation constant.

In aqueous solutions, hydroxide ion is characterized by a large diffusion coefficient,[1,18] its value being the second highest after that of hydronium. Therefore, by analogy with the hydronium reduction process, the OH^- oxidation can be used to examine the effects of ionic strength on mass transport properties. Since an hydroxide ion is a charged species, its voltammetric behavior is expected to depend on the concentration of supporting electrolyte in solution, as the migratory component in the mass transport may play an important role.[19,20] To our knowledge, there is no investigation of the oxygen evolution reaction in aqueous solutions with little or no supporting electrolyte.

In this paper, we present the results of a study on the oxidation process of hydroxide ions at gold microdisk electrodes in the absence and in the presence of different concentrations of supporting electrolyte. In this investigation, we particularly wish to understand the effect of both concentration and nature of the supporting electrolyte on the steady-state limiting current obtained from oxidation of basic solutions prepared with the strong bases NaOH and $Ba(OH)_2$. In addition we wish to consider whether the steady-state limiting current can be predicted from theoretical treatments that account for both diffusive and migratory components in the mass transport. In particular, theoretical relationships derived in the framework of existing theories, Oldham's treatments,[20,21] will be considered. Another objective of this paper is to verify the usefulness of the current for analytical purposes and in particular to check whether amperometry can be utilized to evaluate the pH of basic solutions made with strong bases.

EXPERIMENTAL SECTION

Voltammetric experiments were carried out with a two-electrode cell located in a Faraday cage made of aluminum sheets. The working electrodes were 12.5- and 5-μm-radius gold microdisks, prepared by sealing 25- and 10-μm-diameter gold wires directly in glass. The electrodes were polished with graded alumina powder of different sizes (1, 0.3, and 0.05 μm) on a polishing microcloth. The effective electrode radii of the exposed disks were calculated with eq 1[23−25] after recording the steady-state limiting currents in a 1 mM ferrocene solution in acetonitrile

$$I_d = 4nFDc^b a \tag{1}$$

($D = 2.5 \times 10^{-5}$ cm^2 s^{-1} [22]) I_d is the diffusion-controlled limiting current and a the radius of the microdisk; the other symbols have their usual meaning. The electrode radii measured electrochemically differed by no more than 10% with respect to those determined by optical inspection with an inverted microscope (Litze Wetzlar). Linear sweep voltammetric experiments were controlled by a PAR 175 function generator. A Keithley 428 picoammeter was used to measure the current and data were plotted with a Hewlett-Packard 7045 B $X-Y$ recorder. Unless otherwise stated, the experiments were performed using a Pt pseudoreference electrode. A Metrohm 605 pH meter was employed for pH measurements. The combination pH glass electrode with an Ag|AgCl internal reference electrode and a KCl bridge was purchased from Metrohm; according to the manufacturer, it provides a negligible alkaline error up to pH 12.5. Prior to each series of experiments, the pH meter was calibrated using two standard pH buffer solutions.

All the chemicals employed were of analytical-reagent grade. All the aqueous solutions were prepared with Milli-Q water, which was freshly boiled and stored under a nitrogen atmosphere. Carbonate-free concentrated sodium hydroxide solutions (from Baker) diluted to 1 L, to obtain volumetric standard 0.1 M solutions, were stored in polythene bottles and maintained under a nitrogen atmosphere. To verify the absence of carbonate, the solutions were tested daily by adding an excess of a concentrated solution of barium chloride to aliquots of solution.[26] The presence of carbonate was indicated by the formation of a barium carbonate precipitate. Only those solutions that did not produce a precipitate were employed for the voltammetric experiments. Carbonate-free barium hydroxide solutions were prepared by rapidly filtering the commercially available 0.1 M barium hydroxide (Baker) through a sintered glass funnel.[26] The solutions thus prepared were stored in polythene bottles and maintained under a nitrogen atmosphere. All the basic solutions were standardized by acid−base titrations.[26]

Unless otherwise stated, the measurements were carried out at room temperature after deoxygenating the solutions with a stream of water-saturated CO_2-free nitrogen.

To approach steady-state limiting conditions, a scan rate, ν, of 5 mV s^{-1} was employed in all the experiments. In fact, in the worse case, $a = 12.5$ μm, $D \sim 5 \times 10^{-5}$ cm^2 s^{-1}, and $T = 303$ K (see later); the parameter $p = (nF\nu a^2/DRT)^{1/2}$ [27] is equal to 0.077. Under these conditions, the diffusion limiting current should not exceed the steady-state value by more than 1%.[27] The steady-state limiting current was evaluated at a fixed potential within the potential range corresponding to the plateau, assuming as the baseline that drawn from the residual current recorded before the onset of the wave. All steady-state current data points are mean values of at least three replicates (the relative standard deviation was ~3%).

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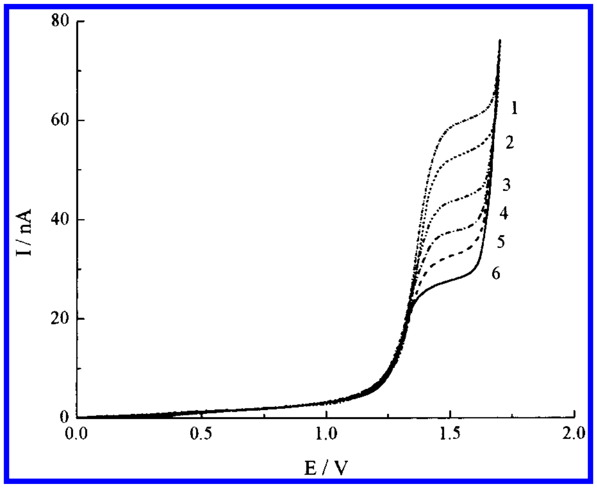

Figure 1. Steady-state voltammograms recorded at 5 mV s^{-1} with a 12.5-μm-radius gold microdisk in 1.50 mM NaOH solutions with (1) no added electrolyte or with the following concentrations of $NaClO_4$: (2) 1.0 × 10^{-4}; (3) 1.03 × 10^{-3}; (4) 1 × 10^{-2}; (5) 0.1; (6) 0.2 M.

Table 1. Half-Wave Potentials Recorded in Aqueous Solutions of Different Composition at a 12.5- and a 5-μm Electrode Radius

solution composition	$E_{1/2}$ vs Pt/V $r = 12.5\ \mu$m	 $r = 5\ \mu$m
1.05 mM NaOH	1.390	1.410
1.05 mM NaOH + 1.02 mM $NaClO_4$	1.380	
1.05 mM NaOH + 1.05 mM Na_2SO_4	1.370	1.390
1.05 mM NaOH + 0.1 M $NaClO_4$	1.360	
1.05 mM NaOH + 0.1 M Na_2SO_4	1.340	1.370
0.52 mM $Ba(OH)_2$	1.390	
0.52 mM $Ba(OH)_2$ + 1.03 mM $NaClO_4$	1.360	
0.52 mM $Ba(OH)_2$ + 0.1 M $NaClO_4$	1.350	

Although they were of analytical grade, the chemicals used to make up the solutions likely contained some impurities, as for instance chloride ions, which may have acted as electrolyte. We were not able to quantify the level of impurities introduced with the solute. However, from typical concentrations stated on the labels for Cl^- (<5 ppm), we could estimate that no more than 8 μM of the latter species was introduced in the solution over the entire concentration range of strong bases employed. Instead, the background electrolyte concentration was calculated from the conductivity of the pure water employed to prepare the solutions. It was measured in the electrochemical cell before each series of measurements and values ranging between 1 and 6 μS cm^{-1} were found. Thus, from the above conductivity values, a solution with no deliberately added supporting electrolyte was equivalent to a solution containing a concentration of KCl varying between 7 and 40 μM. These concentration values will be employed later to calculate the supporting electrolyte to the electroactive concentration ratios.

RESULTS AND DISCUSSION

Dependence of the Steady-State Limiting Current on Ionic Strength. Figure 1 shows typical steady-state voltammograms recorded with a 12.5 μm-gold microdisk electrode for the oxidation of sodium hydroxide solutions in the absence and with different concentrations of $NaClO_4$. The potentials of these waves are quoted against a Pt pseudoreference electrode. Comparative measurements performed in 0.1 M $NaClO_4$ with an Ag|AgCl reference electrode showed that the half-wave potential was ~60 mV more negative than with the Pt pseudoreference electrode.

The voltammograms shown in Figure 1 follow the expected sigmoidal shape, but the steady-state limiting current clearly decreases when the concentration of supporting electrolyte increases. Voltammetric waves very similar to those of Figure 1 were obtained from solutions containing sodium hydroxide with a range of sodium sulfate concentrations and barium hydroxide with different sodium perchlorate concentrations. The half-wave potentials obtained from some of the solutions investigated are shown in Table 1. From this table it is clear that, at given concentrations of supporting electrolyte and hydroxide ions, the half-wave potential values do not differ by more than 20 mV, regardless of the nature of the supporting electrolyte and base employed. This suggests that the species involved in the oxidation process is probably the same, conceivably the hydroxide ion.

To investigate the effects of the electrode radius on the oxidation of hydroxide ion at different concentrations of supporting electrolyte, a series of measurements was carried out using a 5-μm-radius gold microdisk electrode. Solutions containing sodium hydroxide with different concentrations of sodium sulfate were examined. The general voltammetric behavior did not differ from that displayed in Figure 1. Also, the position of the wave, at the same solution composition, was close to that recorded with the bigger electrode. This can be seen from the half-wave potentials obtained with the smaller electrode and included in Table 1. As with the large microdisk, the wave height decreased when the concentration of supporting electrolyte increased. At given concentrations of hydroxide ions and supporting electrolyte, the wave height was ~0.4 times that recorded with the 12.5-μm-radius microdisk. This suggests that the oxidation process of hydroxide ion is under mass transport control.

The overall electrode process for the oxidation of hydroxide ions can be written as follows:

$$OH^- \rightarrow {}^1/_4O_2 + {}^1/_2H_2O + e^- \qquad (2)$$

The current plateau is located in the foot of the oxygen evolution process due to the solvent; however, within the potential range corresponding to the plateau, the production of oxygen by the electrode did not lead to the formation of bubbles. In fact, no current oscillation was observed in the voltammograms. We attribute this to the fast removal of the oxygen formed in the reaction, by the quasi-hemispherical diffusion. Because of the larger current involved, bubbles were probably formed at more positive potentials, where the current became oscillatory.

Figure 2 shows the dependence of the steady-state limiting current on the concentration of hydroxide ions in various aqueous solutions: without supporting electrolyte, with 0.1 M $NaClO_4$, and with 0.1 M Na_2SO_4. The full lines represent the best fit obtained by linear regression analysis of the experimental points. The correlation coefficients for all these plots were greater than 0.9995. In 0.1 M supporting electrolyte, the straight lines produce slopes that are very close to one another, the average value being 18.9 (±0.4) nA mM^{-1}.

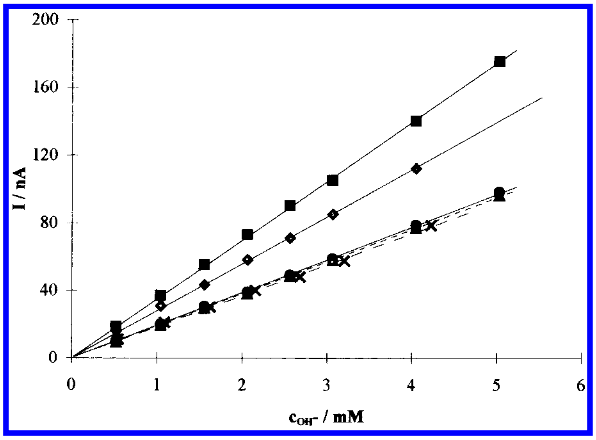

Figure 2. Limiting current versus the concentration of hydroxide ions for NaOH with (■) no electrolyte, (●) Na_2SO_4 0.1 M, and (△) $NaClO_4$ 0.1 M; and for $Ba(OH)_2$ with (◇) no electrolyte and (×) $NaClO_4$ 0.1 M.

In solutions with no deliberately added supporting electrolyte, the slope of the plot obtained using sodium hydroxide is 34.8 nA mM^{-1}, while that obtained using barium hydroxide is 27.8 nA mM^{-1}. The ratios of the slopes obtained in solution with no deliberate addition of supporting electrolyte to those in excess of supporting electrolyte are 1.8 and 1.5, for solutions prepared with NaOH and $Ba(OH)_2$, respectively.

The hydroxide ion is a negatively charged species which oxidizes to a neutral product while the accompanying cation is either a univalent (Na^+) or a divalent species (Ba^{2+}). In the absence of supporting electrolyte, the migration flux is significant and the limiting current is predicted to be twice the diffusion current for solutions made with NaOH or 1.5 times the diffusion current for $Ba(OH)_2$ solutions.[19] The experimental values (1.8 and 1.5) are therefore close to the theoretical predictions.

Voltammograms 5 and 6 in Figure 1 were recorded in conditions which should ensure that diffusion controls mass transport,[19,20] yet the steady-state limiting current is found to decrease for supporting electrolyte concentrations greater than 0.1 M. This variation is not due to migration since the concentration of supporting electrolyte is almost 67 times larger than that of the hydroxide ion; instead it probably reflects the dependence of the diffusion coefficient on both ionic strength and viscosity.[28] We evaluated these aspects in detail and derived theoretical equations to predict the variation of the steady-state current with the supporting electrolyte concentration over a wide range.

The method proposed by Oldham and Myland[19−21] was considered to treat the transport of the species in the solution. Assuming spherical mass transport, a common assumption for microdisk electrodes,[25] the general material balance relationship can be written as

$$\frac{dc_i}{d(1/r)} + z_i c_i \frac{F}{RT}\frac{d\Phi}{d(1/r)} = \frac{I\nu_i}{2\pi nFD_i} \qquad (3)$$

where c_i, D_i, z_i, and ν_i are respectively the concentration, the diffusion coefficient, the charge number, and the stoichiometric coefficient of species i, $d\phi/dr$ is the potential gradient, and I is the steady-state current. This equation applies to each of the solute species present in the solution, either electroactive or electroinactive. Considering reaction 2 and the different species involved in the solutions studied, the coefficient ν_i respectively takes the values 1 and $^1/_4$ for OH^- and O_2 and 0 for Na^+, Ba^{2+}, ClO_4^-, and SO_4^{2-}, which are electroinactive.[21] Assuming that electroneutrality is maintained throughout the solution, a system of eqs 3, one for each species present, is formed which can be solved analytically to give the concentration profile of each species. At an overpotential sufficient to allow complete polarization, i.e., so that the concentration of OH^- is zero at the electrode surface, the following equations

$$I_{lm}/I_{ld} = 2 + 2\rho - 2[\rho(1+\rho)]^{1/2} \qquad (4)$$

$$I_{lm}/I_{ld} = 2 + 3\rho - 3[(1/4)\rho + \rho^2 + \rho^3]^{1/3} \qquad (5)$$

were found for NaOH in the presence of $NaClO_4$ and Na_2SO_4, respectively. A rather elaborate implicit expression was derived for $Ba(OH)_2$ in the presence of $NaClO_4$:

$$[2\rho^2 + 2\rho N + (3/2)M][2\rho - N] + (9/2)[\rho + N]M + (27/4)\rho = 0 \qquad (6)$$

where $N = (\rho^2 + M)^{1/2}$ and $M = [-I_{lm}/I_{ld} + (3/2) + 2\,\rho]$. I_{lm}/I_{ld} is the ratio of the limiting current, I_{lm}, to the diffusion-controlled limiting current, I_{ld}. ρ is the "support ratio" defined as $\rho = c_S^b/c_{OH^-}^b$, that is the ratio of the concentration of the supporting electrolyte added c_S^b, to the concentration of the electroactive species $c_{OH^-}^b$. These equations yield current ratios identical to those found for the reduction of a monovalent cation.[20,29,30]

To predict the change of diffusion coefficient with ionic strength we used a theoretical treatment based on[28]

$$D = D_0(1 - (k/2)\sqrt{S}) \qquad (7)$$

where D and D_0 are respectively the diffusion coefficients of the electroactive species in the presence of supporting electrolyte and at infinite dilution, k is a constant that depends on both the nature of the medium and temperature (for water, k^{28} respectively equals 0.5070, 0.5115, and 0.5161 $M^{-1/2}$ at 293, 298, and 303 K), and S is the ionic strength. To correct the steady-state limiting current from diffusion coefficient effects, we employed the dimensionless parameter $\Delta(S) = D/D_d$, i.e., the ratio of the diffusion coefficient at a given ionic strength, D, to the diffusion coefficient, D_d, corresponding to the reference diffusion-limiting current I_{ld}. Recalling eq 7, one obtains

$$\Delta(S) = \frac{D_0}{D_d}(1 - (k/2)\sqrt{S}) \qquad (7)$$

Since $D_d = D_0(1 - (k/2)S_d^{1/2})$, where S_d is the reference ionic

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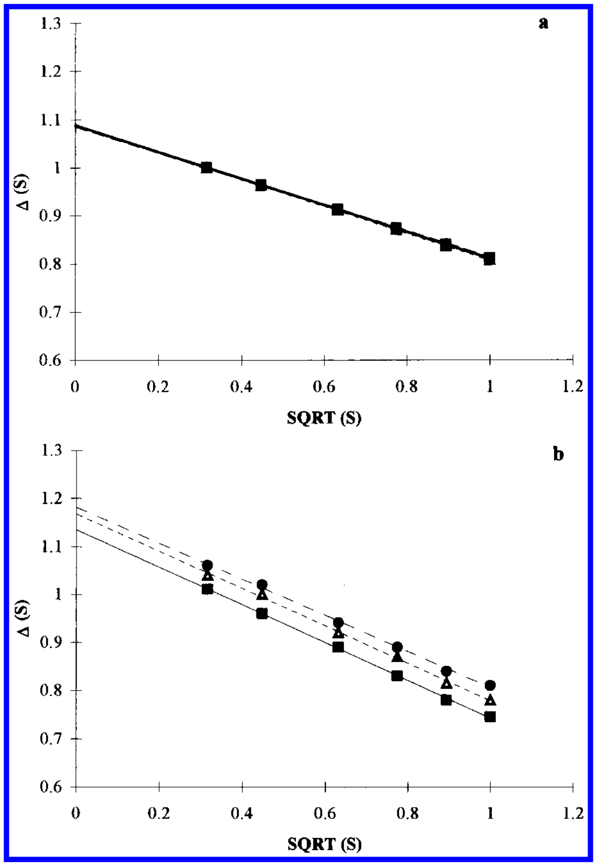

Figure 3. Plots of the dimensionless parameter Δ(S) against the square root of ionic strength: (a) theoretical dependence at (■) 293, (●) 298, and (△) 303 K; (b) experimental dependence determined in 1.05 mM NaOH solutions and $NaClO_4$ supporting electrolyte at (■) 293, (●) 298, and (△) 303 K.

strength, eq 8 can be written as:

$$\Delta(S) = (2 - k\sqrt{S})/(2 - k\sqrt{S_d}) \qquad (9)$$

Equation 9 suggests that a plot of $\Delta(S)$ vs $S^{1/2}$ should give a straight line with slope $-k/(2 - kS_d^{1/2})$ and intercept $2/(2 - kS_d^{1/2})$.

To assess the validity of the theoretical predictions, an empirical dependence of the diffusion coefficient with ionic strength was evaluated from measurements of steady-state limiting currents in solutions containing enough supporting electrolyte so that migration contributes negligibly to the mass transport. It can be easily demonstrated that the ratio of limiting currents at each concentration of supporting electrolyte to the reference diffusion limiting current, I_{ld}, is equal to $\Delta(S)$. Consequently, a plot of the experimental current ratios against the square root of the ionic strength is expected to produce a linear trend whose equation can be used to evaluate $\Delta(S)$ at any ionic strength including that at which migration applies. We evaluated the experimental dependence of $\Delta(S)$ on $S^{1/2}$ with a solution containing 1.05 mM NaOH and varying concentrations of $NaClO_4$ over the range 0.1−1 M, in which the viscosity change is negligible (see later). The reference diffusion limiting current was taken arbitrarily to be that in a 0.1 M solution of indifferent salt.

Table 2. Theoretical and Experimental Equations for $\Delta(S)$ vs $\sqrt{S}$

	equations	
T/K	theoretical	experimental
293	$\Delta(S) = -0.286\sqrt{S} + 1.091$	$\Delta(S) = -0.393\sqrt{S} + 1.14$
298	$\Delta(S) = -0.278\sqrt{S} + 1.088$	$\Delta(S) = -0.376\sqrt{S} + 1.18$
303	$\Delta(S) = -0.271\sqrt{S} + 1.086$	$\Delta(S) = -0.389\sqrt{S} + 1.17$

Table 3. Theoretical (th) and Experimental (exp) Diffusion Coefficients for the Hydroxide Ion at Different Temperatures and at Different Ionic Strengths[a]

T/K	D_0^{th}/ $\times10^{-5}$ cm^2 s^{-1}	D_0^{exp}/ $\times10^{-5}$ cm^2 s^{-1}	D_d^{th}/ $\times10^{-5}$ cm^2 s^{-1}	D_d^{exp}/ $\times10^{-5}$ cm^2 s^{-1}
293	4.74	4.88	4.34	4.32
298	5.23	5.19	4.80	4.62
303	5.76	5.58	5.30	4.98

[a] D_0^{th} calculated by eq 10 at infinite dilution; D_d^{th} calculated by eq 7 at 0.1 M ionic strength; D_0^{exp} determined by extrapolation at zero ionic strength from the straight lines of Figure 3b; D_d^{exp} determined from steady-state limiting currents in 0.1 M $NaClO_4$.

Figure 3 shows theoretical (calculated with eq 9) and experimental $\Delta(S)$ versus $S^{1/2}$ plots at three temperatures. Table 2 shows the relevant linear equations. The theoretical plots are very similar to one another (see Figure 3a), whereas in all the experimental plots, intercepts, and slopes are larger than those calculated theoretically (see Table 2). However, diffusion coefficients determined in 0.1 M supporting electrolyte from the diffusion limiting currents and eq 1, and at zero ionic strength from extrapolation of the straight lines in Figure 3b, agree within 10% with theoretical values (see Table 3). Theoretical D_0 values were determined with the equation proposed by Nernst:[31]

$$D_0 = 8.96 \times 10^{-10} T\lambda_0/z \quad \text{in cm}^2\ \text{s}^{-1} \qquad (10)$$

where λ_0 is the equivalent conductance at infinite dilution, T is the absolute temperature, and z is the charge number of the ion.

The dependence of the diffusion coefficient with viscosity can be accounted for by the following equation:[28]

$$D = k_B T/6\pi\eta r_h \qquad (11)$$

where k_B is the Boltzmann constant, T is the temperature (in K), η is the absolute viscosity, and r_h is the hydrodynamic radius of the diffusing species. The diffusion coefficient at a given ionic strength was corrected for viscosity effects by the factor η/η_d, the ratio of the viscosity of the solution at the given ionic strength, η, to that at 0.1 M of the indifferent salts, η_d. For the electrolyte solutions examined here, the maximum values of η/η_0 (η_0 is the viscosity of pure water) at 298 K over the concentration range 0−1 M are 1.044 [32] and 1.62 [33] for $NaClO_4$ and Na_2SO_4, respec-

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tively. For the latter salt, however, the maximum value is 1.039 [33] over the concentration range 0−0.1 M. The variations of diffusion coefficients due to viscosity can be considered negligible (within 4%) for $NaClO_4$ solutions over all the concentration range explored in this paper (0−1 M) and for Na_2SO_4 over the range 0−0.1 M.

Considering the above effects altogether, the variations of steady-state limiting current with the concentration of supporting electrolyte can be conveniently written in the following abbreviated form:

$$I_{\rm lm}/I_{\rm ld} = \Delta(S)\Delta(\rho)\Delta(\eta) \qquad (12)$$

where $\Delta(\rho)$ is the right-hand side term in the eqs 4−6 and $\Delta(\eta) = \eta/\eta_{\rm d}$.

Theoretical relationships based on eq 12 for the different systems examined here are displayed in Figure 4. These refer to a temperature of 298 K. However, for each solution and for a given concentration of hydroxide ions, theoretical plots calculated at 293, 298, and 303 K overlapped within 1% and 4% depending on whether they were evaluated with the theoretical or empirical $\Delta(S)$ relationship. This means that measurements taken at room temperature, which usually fall within the above interval, are not distinguishable from one another, as the theoretical differences are close or within the relative experimental error made in the evaluation of the limiting current (3%). The solid, dashed, and dotted lines shown in Figure 4 correspond to different initial concentrations of the electroactive species. The slight shift on the X axis arises because the ionic strength is related to the support ratio according to $S = c^{\rm b}_{\rm OH^-}(1 + \rho)$ and $S = c^{\rm b}_{\rm OH^-}(3\rho + 1)$ for $NaClO_4$ and Na_2SO_4 solutions, respectively. Figure 4 also shows that the theoretical current ratio predicted in the absence of supporting electrolyte is larger than 2 for NaOH solutions and than 1.5 for $Ba(OH)_2$ solutions. On the other hand, in solutions with excess of electrolyte, the limiting current ratio is less than 1. This fact reflects the variation of diffusion coefficients with ionic strength. The extent of these differences depends on the choice of the conditions employed for determining the reference diffusion coefficient, $D_{\rm d}$.

Figure 5 compares theoretical (lines) and experimental (points) plots of $I_{\rm lm}/I_{\rm ld}$ versus log ρ at a given concentration of NaOH (1.50 mM) or $Ba(OH)_2$ (1.00 mM). Since the solutions contain electrolytic impurities, the support ratio for the experimental plots was evaluated as $\rho = (c^{\rm b}_{\rm S} + c^{\rm b}_{\rm B})/c^{\rm b}_{\rm OH^-}$, to take into account the concentration of the background electrolyte $c^{\rm b}_{\rm B}$ obtained from conductivity measurements (see Experimental Section). The two theoretical plots (corresponding to the empirical and theoretical methods used to estimate $\Delta(S)$) obtained in $NaClO_4$ differ to some extent (within 8%), while those in Na_2SO_4 almost overlap (within 1.5%). This would indicate that data obtained in sodium sulfate are less sensitive to errors made in the experimental evaluation of the dependence of the diffusion coefficient on the ionic strength. This effect is actually a consequence of the difference in ionic strength between sodium perchlorate and sodium sulfate supporting electrolytes (for a given concentration of the supporting electrolyte the ionic strength due to sodium sulfate is ~3 times larger than that with sodium perchlorate). It must be noted that to calculate the ionic strength of sodium sulfate it was assumed, for the sake of simplicity, that the salt was completely dissociated at any concentration. As a matter of fact, at high sodium sulfate concentrations, the species $NaSO_4^-$ can be formed to a considerable extent. From stability constants available in the literature[34] ($K = 10^{0.3}$ M^{-1}, at $S = 0.5$ M), it was verified that the concentration of the above species is lower than 2% up to ~0.01 M disodium sulfate; it is 9% at 0.1 M and increases up to ~30% at 1 M disodium sulfate. Since the migration effect is negligible for sodium sulfate concentrations larger than 0.01 M, the formation of the species $NaSO_4^-$ should affect only the ionic strength, this being lower than that predicted assuming the salt is completely dissociated.

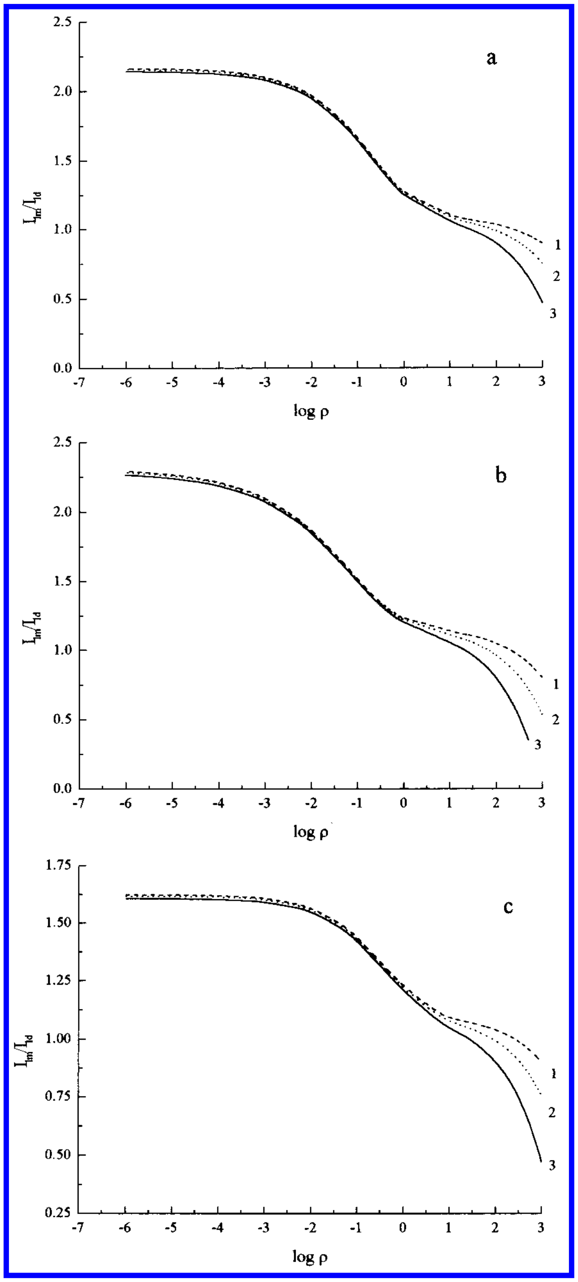

Figure 4. Theoretical dependence of the limiting current ratios versus the concentration of the supporting electrolyte added. Chemical composition of the solutions: (a) NaOH with $NaClO_4$; (b) NaOH with Na_2SO_4; (c) $Ba(OH)_2$ with $NaClO_4$. Initial concentration of hydroxide ion $c^{\rm b}_{\rm OH^-}$: (1) 0.52, (2) 1.50, AND (3) 4.99 mM.

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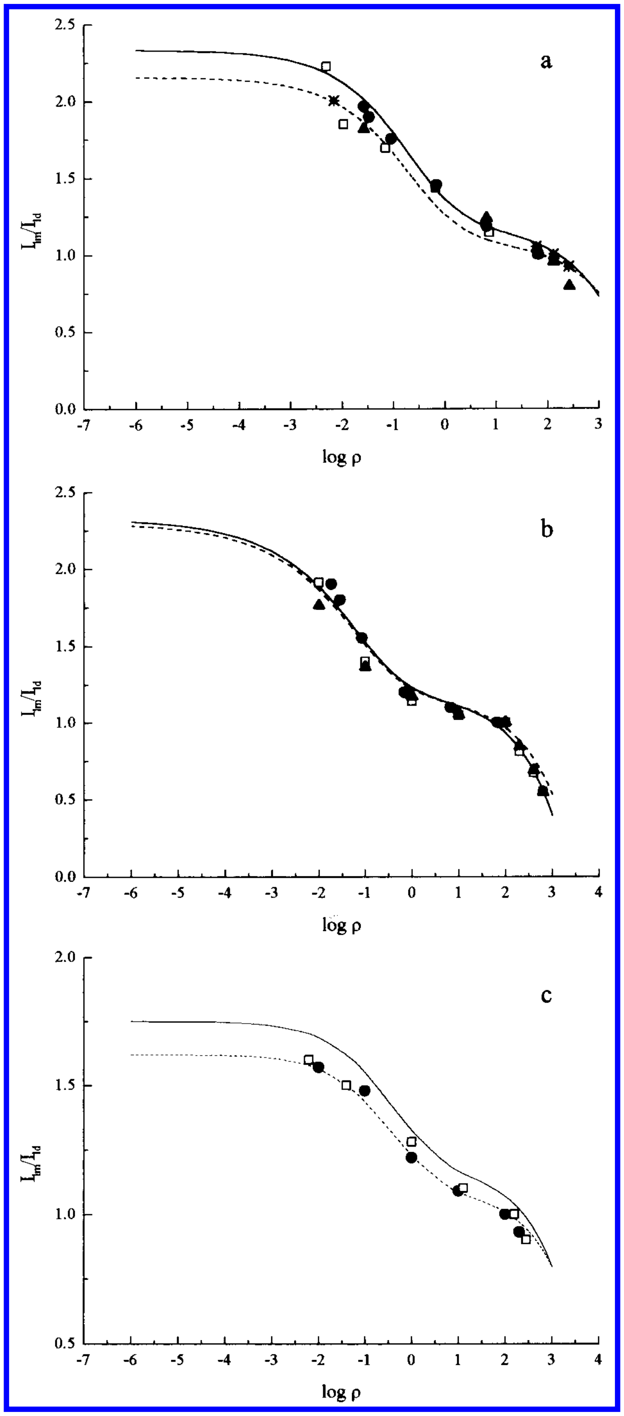

Figure 5. Comparison between theoretical (lines) and experimental (symbols) plots of the limiting current ratios versus the concentration of supporting electrolyte present in the solution. Theoretical (dashed lines) and experimental (solid lines) determination of the relationship between *D* and *S*. (a) NaOH 1.50 mM with $NaClO_4$ at 298 (●), 299 (▲), 295 (□), and 294 K (∗); gold microdisk 12.5-μm radius. (b) NaOH 1.50 mM with Na_2SO_4 at 298 (□) and 297 K (●); gold microdisk 12.5-μm radius. NaOH 1.5 mM with Na_2SO_4 at 298 K (▲); gold microdisk 5-μm radius. (c) $Ba(OH)_2$ 0.52 mM with $NaClO_4$ at 2930 (□) and 294 K (●); gold microdisk 12.5-μm radius.

It also follows that the diffusion coefficient dependence (through eq 7) on the salt concentration may be different. However, we calculated that, in 0.1, 0.5, and 1 M sodium sulfate, the diffusion coefficients evaluated by neglecting the formation of the complex species are respectively 0.5%, 5%, and 11% smaller than those calculated taking into account ion pairing between Na^+ and SO_4^{2-}. Thus, the error made is lower than 11%, which is satisfactory for diffusion coefficient evaluation.

In all the plots shown in Figures 4 and 5, the reference diffusion coefficient values were evaluated at 0.1 and 0.3 M ionic strength in $NaClO_4$ and Na_2SO_4 solutions, respectively. Experimental plots in Figure 5 were determined at room temperatures, over the range 273−303 K. Despite some scatter, the data follow the theoretical prediction given by eq 12.

Relationship between pH and Steady-State Limiting Current. There exist several situations where the determination of pH by classical potentiometric methods is not possible. These include probing pH in the vicinity of an electrode,[35] over a polymeric matrix,[36] or in colloidal solutions.[37] In acidic solutions, the reduction of hydronium ions can be employed as an alternative to potentiometric methods.[35−37] The possibility of evaluating the pH of basic solutions by exploiting the voltammetric wave for the oxidation of hydroxide ions is discussed here.

Steady-state limiting current and pH are actually related to two different quantities; while the steady-state limiting current is related to the concentration of hydroxide ions, pH is related, through the autoprotolysis constant of water, to its activity. Therefore, the following equation holds:

$$\mathrm{pH} = \log c_{\mathrm{OH^-}} + \log \gamma_{\mathrm{OH^-}} - \log K_{\mathrm{w}} \tag{13}$$

where $c_{\mathrm{OH^-}}$ and $\gamma_{\mathrm{OH^-}}$ are respectively the concentration and the activity coefficient of OH^- and K_w is the water autoprotolysis constant. Provided that the oxidation wave due to hydroxide is mass transport controlled (as shown by the results presented here), $c_{\mathrm{OH^-}}$ at a given ionic strength, can be calculated from eq 12. Considering that the diffusion limiting current is given by eq 1, after expressing concentrations in moles per liter one obtains

$$\mathrm{pH} = \log\left\{\frac{10^3 I_m}{4FD_{\mathrm{d}}a\Delta(S)\Delta(\rho)}\right\} + \log \gamma_{\mathrm{OH^-}} - \log K_{\mathrm{w}} \tag{14}$$

To calculate pH values, the activity coefficient of hydroxide ion as well as the equilibrium constant of water at different ionic strength must be known. Theoretical individual activity coefficient values for hydroxide ion were evaluated from the Debye−Hückel equation, while K_w at various ionic strengths were evaluated by interpolating data available from the literature.[34]

Table 4 shows experimental (measured with a pH meter) and calculated (from the concentration of hydroxide ions measured amperometrically) pH values for several aqueous solutions of sodium hydroxide containing different amounts of supporting electrolyte. At a given concentration of base, the pH changes owing to the variation of the ionic strength of the solution. This is in agreement with what one expects. For the calculated values, the variation is due to the change of activity coefficient and dissociation constant of water with ionic strength. In addition to the above effects, the experimental values include the variation

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Table 4. Comparison between Experimental (exp) and Calculated (th) pH Values Obtained from Aqueous Solutions Containing Different Concentrations of both NaOH and $NaClO_4$[a]

c^b_{NaOH}/M	$c^b_s + c^b_B$/M	I ($\pm 0.05 \times 10^{-8}$)/ $\times 10^{-8}$ A	pH_{exp} (± 0.02)	$\Delta(S)$	$\Delta(\rho)$	γ_{OH^-}	pH_{th}	ΔpH
4.1×10^{-4}	1.1×10^{-5}	1.80	10.45	1.082	1.504	0.976	10.66	−0.21
8.5×10^{-4}	1.1×10^{-5}	3.50	10.85	1.080	1.599	0.967	10.92	−0.07
1.30×10^{-3}	1.1×10^{-5}	5.30	11.10	1.079	1.646	0.960	11.08	0.02
1.50×10^{-3}	3.5×10^{-5}	5.55	11.20	1.078	1.738	0.957	11.08	0.12
1.50×10^{-3}	2.2×10^{-5}	4.90	11.12	1.152	1.584	0.956	11.04	0.08
1.50×10^{-3}	1.1×10^{-4}	4.50	11.16	1.151	1.353	0.953	11.07	0.09
1.50×10^{-3}	1.00×10^{-3}	3.80	11.18	1.143	1.095	0.930	11.07	0.11
1.50×10^{-3}	1.0×10^{-2}	3.05	11.06	1.111	1.012	0.841	10.92	0.14
1.50×10^{-3}	4.5×10^{-5}	5.30	11.10	1.078	1.708	0.957	11.07	0.03
1.50×10^{-3}	1.4×10^{-4}	4.90	11.08	1.077	1.554	0.956	11.07	0.01
1.50×10^{-3}	1.10×10^{-3}	4.05	11.13	1.075	1.220	0.945	11.09	0.04
1.50×10^{-3}	1.1×10^{-2}	3.30	11.08	1.059	1.035	0.894	11.03	0.05
1.50×10^{-3}	1.1×10^{-1}	2.80	11.01	1.000	1.004	0.760	10.74	0.27
1.30×10^{-3}	0.39	2.30	10.99	0.911	1.000	0.645	10.79	0.20
1.30×10^{-3}	0.59	2.15	10.83	0.871	1.000	0.612	10.76	0.07
1.30×10^{-3}	0.80	2.00	10.83	0.838	1.000	0.591	10.73	0.10
1.30×10^{-3}	0.98	1.85	10.75	0.808	1.000	0.574	10.70	0.05

[a] $\Delta pH = pH_{(exp)} - pH_{(th)}$. Other symbols as in the text.

of liquid junction potential due to the difference between the salt solution of the investigated medium and that of the standard buffer solutions used to calibrate the instrument.[38] The influence of the liquid junction potential for the common glass combination electrode is not easily predictable. This has been discussed in several papers and it appears to be a continuing problem.[38−41] We can speculate that the liquid junction potential effect may be a reason for the marked differences observed in some cases between measured and calculated pH values. In many cases, however, the agreement between experimental and calculated values is good. Overall, considering all the above factors, we may conclude that the agreement between potentiometrically and amperometrically determined pH values is satisfactory. A comment must be made regarding the practical exploitation of these measurements. The most useful conditions for determining pH by amperometry are those corresponding to solutions containing a sufficient excess of indifferent electrolyte so that $\Delta(\rho) \approx \Delta(S) \approx 1$ in eq 14. For instance, for pH values around 11, a 0.01 M concentration of indifferent 1:1 electrolyte, or 0.001 M for a 2:1 electrolyte (or for a base such as $Ba(OH)_2$), is sufficient.

Finally, it must be noted that no restriction has been imposed to derive eq 14. Thus, it can be extended to more complex media, provided that proper ionic strength and equilibrium constants are employed in the latter equation.

CONCLUSIONS

The electrochemical process for oxygen evolution involves the formation of oxides at the electrode surface and is therefore much more complex than that described in eq 2. Yet the findings presented here indicate that the waves shown in Figure 1 for the oxidation of hydroxide are essentially mass transport controlled; moreover, the analysis confirms that one electron is involved in the overall oxidation process. The current associated with the formation of oxides at the electrode surface, which appears to a large extent to represent the main process observed with classical conventional electrodes, becomes negligible with microelectrodes under a steady-state regime. The formation of oxides occurs at less positive potentials[42−44] and therefore cannot be mixed with the redox reaction described in the present paper.

The present study has also shown that the oxidation of hydroxide ions under steady-state conditions with gold microelectrodes provides an alternative method for the determination of pH in basic solutions. Since these data are free from junction potential effects, in principle, the steady-state voltammetric approach can be employed to calibrate a glass electrode in basic solutions.

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