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pH MEASUREMENT IN STRONG KOH SOLUTIONS WITH A BISMUTH ELECTRODE

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Abstract—Bismuthized platinum electrodes were investigated as pH indicating electrodes in strong KOH solutions (pH 14–16). The E–pH curve of freshly prepared bismuth electrodes is linear, but the E–pH slope altered with time. It is shown that the slope is constant if the bismuth electrode has been aged via immersion in a concentrated KOH solution. The value of the E–pH slope depends on the KOH concentration of the ageing electrolyte; a higher KOH concentration resulting in a less negative value of the E–pH slope. The pH of strong alkaline solutions can be monitored with these electrodes for several hours.

The bismuth electrode surface morphology and composition were studied with ESCA and SEM techniques. It is suggested that at freshly prepared bismuth electrodes the formation of the bismuth trioxide or trihydroxide is the potential determining process. At aged electrodes, the potential determining process may involve various bismuth oxide species, but a reaction occurring via the solution cannot be excluded.

INTRODUCTION

The acidity of an aqueous solution can easily and accurately be determined with a pH indicating electrode if the value of the pH is in the range from 2 to 12. However, many problems are encountered when the pH in strong alkaline solutions is to be measured. Experimentally, the alteration of pH due to carbon dioxide incorporation of the electrolyte and errors due to the occurrence and extent of liquid junction potentials are not easy to estimate. Also, the uncertainty in the calibration of the electrode, due to unknown or not accurately known values of the activity coefficient determines the accuracy of the pH measurement. Few investigators[1, 2] tried to cope with these problems, none could surmount them all.

The aim of this investigation is to develop a pH indicating electrode of small dimensions which can be used in strong KOH solutions to monitor local pH changes.

HYDROGEN-ION SENSITIVE ELECTRODES FOR ALKALINE SOLUTIONS

pH-indicating electrodes can be classified into three groups: (1) the hydrogen-ion sensitive membrane electrodes; (2) the metal–metal oxide electrodes; (3) the Ion Sensitive Field Effect Transistor (ISFET) electrodes.

The glass electrode (group 1) is one of the most thoroughly studied electrodes[3–5], and can be used in the pH range from 2 to 12. Recently, Licht[2] investigated the behaviour of a low alkali-error glass electrode in strong alkaline electrolytes (up to 17 molal potassium hydroxide). With the aid of a cation-selective electrode he could estimate the alkali error and correct the measured pH value. With this procedure he claimed that the pH can be measured with an accuracy of 0.1 pH units.

As an alternative for glass electrodes, metal–metal oxide electrodes are often suggested. Many metal–metal oxide electrodes have been studied on their pH response and a number of them have been used successfully.

Two types of metal–metal oxide electrodes can be distinguished. For type I the formation of the oxide of the metal is responsible for the pH-dependence of the electrode potential:

\[
Me + nH,O \rightleftharpoons MeO_n + 2nH^+ + 2n\text{e}^-. \quad (1)
\]

Examples of this type are the mercury–mercuric oxide, the antimony and the bismuth electrode. For the type II electrodes the response to pH is governed by the sensitivity of the oxide towards changes in hydrogen or hydroxyl ion concentration. The pH response mechanism of type II electrodes include ion exchange and different kinds of redox reactions. Examples of this type are the IrO$_2$, the PtO$_2$ and the TiO$_2$ electrode.

The mercury–mercuric oxide[1] and the antimony electrode[6–8] are commonly used, but both are found to be applicable only over a limited pH range. For the Hg/HgO electrode, a Nernstian response is found for pH values greater than ten[3]; no pH upper limit for the use of this electrode has been found. Szabo et al.[1] have studied the behavior of a Hg/HgO electrode in alkaline electrolytes of constant ionic strength. The pH dependence of the open circuit potential of this electrode, measured vs a Hg/HgO electrode in a one molar sodium hydroxide solution, was linear with a slope of $-0.059$ V at $25^\circ$C up to a concentration of six molar sodium hydroxide.

A Nernstian-like behavior of the antimony electrode is limited to pH values ranging from 3 to 10. Outside this range, the solubility of the amphoteric antimonous oxide increases and as a result, the electrode potential changes continuously[6].

Whereas the Hg/HgO electrode is made from a mix of mercury and mercuric oxide, the antimony elec-
trode consists of the metal only. In fact, the presence of the oxide has a deleterious effect on the potential of the electrode, probably due to the formation of higher oxides[6]. Therefore, the antimony electrode is almost always used for short term measurements.

Many other metal–metal oxide systems have been studied, like arsenic[3], tungsten[9, 10], zirconium[10], iron[11], tin[12] and bismuth[13–17]. These electrodes consist of the metal only as was the case with the antimony electrode. The formation of an oxide layer on these electrodes, chemically or electrochemically, seems to passivate the electrodes, resulting in an almost indifferent behaviour towards changes in the alkalinity (acidity) of the solution. Therefore, some investigators used a rotating electrode of which the surface was continuously cleaned with a brush[6, 17], thus ensuring an ‘oxide-free’ surface. The pH dependence of these electrodes was linear over a limited range of pH values. In almost all cases the upper limit was 12. Only bismuth has been used for alkaline solutions up to a pH value of 14[16].

The type II metal–metal oxide electrodes have received much attention in the past two decades. The main application of these electrodes is for high temperature monitoring of pH, though ambient temperature use is also investigated. One of the most promising candidates is the iridium oxide electrode[18, 19]. Other electrodes in research are the palladium[20], zirconium, platinum and titanium oxide electrodes[21]. The preparation of the oxide (chemical oxidation of the metal, decomposition of a salt in the presence of oxygen or electrochemical oxidation) appears to determine the potential of the electrode. Generally, a Nernstian slope is found in the pH range from 2 to 12. Outside this range measurements have not been attempted or were not successful.

Since 1970 when Bergveld[22] showed that semiconductor components could be applied to measure the concentration of chemical species, many investigators have tried to develop hydrogen ion sensitive electrodes with the ISFET technology, mainly for biological and medical applications. These pH indicative electrodes contain SiO₂ or Si₃N₄ as the hydrogen ion sensitive element. Other compounds have been studied which had better characteristics (less voltage drift, better Nernst behavior), like Ta₂O₅ and Al₂O₃[23]. These electrodes were typically used in nearly neutral buffered solutions. No effort has been made to extend the measurement of pH to strong acid or strong alkaline solutions.

Though the low alkali error glass electrode used by Licht[2] and the Hg/HgO electrode developed by Szabo[1] have been applied successfully in strong alkaline solutions, these systems have their disadvantages. For instance the glass electrode can only be used when the alkali error is known for the type of alkali metal and the amount of it under consideration. The Hg/HgO electrode shows a slow response to changes in pH; Szabo found that it took 5 min before attainment of equilibrium could be assumed i.e., before the electrode potential had a usable value. Also, for certain applications the electrodes have to be reduced in size, which presents a problem with these electrodes.

Because of these limitations we investigated the use of small bismuth electrodes in strong alkaline solutions. The bismuth electrode has certain useful properties in alkaline solutions. The metal is relatively noble and the oxide has a low solubility in alkaline media. It can be plated onto a platinum substrate and the platinum can be sealed in glass for mechanical stability, which is important when an electrode of small dimensions is wanted.

Moreover, the potential of the bismuth electrode has been found to be indicative for pH changes up to pH 14[14], although the equilibrium open-circuit potential of the bismuth electrode is only slowly reached.

**EXPERIMENTAL SECTION**

Electrodeposited bismuth electrodes were used in this study. Bismuth was plated onto a platinum substrate from a perchlorate bath, as described by Harbaugh and Mathers[24]. The current density of 100 μA mm⁻² was reduced after one hour to 10 μA mm⁻² to ensure a complete coverage of the electrode. The platinum wires, which had a diameter of 0.7 mm, were sealed in lead glass, with only a surface of about 4 mm² uncovered. The thickness of the electrodeposited bismuth layer was calculated to be about 40 μm. Some of the bismuth electrodes were electrochemically oxidized in solutions of 1 molar potassium hydroxide. The total charge used for oxidation was one tenth of the charge used for the electrodeposition of bismuth, resulting in a thin oxide layer of about 4 μm. These electrodes are indicated as Pt/Bi/BiO₂.

It was observed that the electrode potential changes with time during prolonged standing in alkaline solution. Therefore, we also studied electrodes which have been aged in a potassium hydroxide solution of a certain concentration for at least one week. This type is referred to as Pt/Bi/aged/m, for an electrode aged in a solution of m molal potassium hydroxide.

The alkaline solutions were freshly prepared before each measurement from Analar Grade potassium hydroxide and doubly distilled water. During preparation care was taken to avoid contact with air. Therefore, the error in the KOH concentration due to carbon dioxide incorporation is small.

All cells were made from polyethylene. The temperature during the measurements was 20°C.

The open circuit potential of the bismuth electrode was measured with a voltmeter in combination with an impedance converter. This converter reduced the current in the measuring circuit to at most 0.1 μA. The potential of the bismuth electrodes was measured vs a saturated calomel electrode (sce). The error in the measurement of the potential due to liquid-junction potentials in these electrolytes is estimated to be about 0.001 V[2].

Three methods for measuring the pH-dependence of the potential of the bismuth electrode were used.

(1) The “Fast Hopping Method” (FH-method)

Ten solutions of potassium hydroxide ranging in concentration from one to ten molal were prepared in closed polyethylene cells. An electrode was subsequently immersed in each solution, 5 min before each measurement. On changing the electrode from
one cell to another, both the electrode and the solution were shortly in contact with air. A set of measurements, covering the range from 1 to 10 molal and from 10 to 1 molal, took about 2 h.

(2) The "Slow Hopping Method" (SH-method)

The same technique as in the FH-method was used, but the time between the measurements was longer. The electrode was immersed into a solution and measured after 5 min. It remained in this cell for about 1–1.5 h and was then brought over to another cell with the next higher concentration of potassium hydroxide (after the 10 molal electrolyte the electrode was put in a 1 molal KOH solution).

(3) The "Dilution Method" (D-method)

A concentrated solution of potassium hydroxide was diluted with water by adding small amounts at a time. The solution was stirred for 1 min. The potential of the bismuth electrode was constant after another 2 min. No effort was made to avoid exposure to air.

RESULTS

The pH of concentrated alkaline electrolytes

The pH of a solution is defined as the negative logarithm of the hydrogen ion activity. This definition can be rewritten for alkaline solutions, including the water dissociation constant, $K_w$:

$$\text{pH} = pK_w + \log a_{OH^-} - \log a_w$$

Since the activity of the hydroxyl ion, $a_{OH^-}$, is unknown, the value of pH cannot be calculated with Equation (2). Hence, several colorimetric techniques are employed to measure the pH of strong acid and strong alkaline solutions. However, the acidity functions derived from these experiments do not fit the pH defined by Equation (2). This difference consists of an unknown constant and a pH dependent term, which includes contributions of the indicator ion activity coefficients. Therefore, we used for our calculations Equation (3), which is based upon experimentally known parameters:

$$\text{pH} = pK_w + \log (f_{KOH} m_{KOH}) - \log a_w$$

Though this expression for the pH cannot be derived from thermodynamic arguments, it has been shown[2], that it yields a good estimate of the pH for concentrated KOH electrolytes.

The value of $pK_w$ is 14.17 at 20°C. The mean molal activity coefficient, $f_{KOH}$, and the water activity, $a_w$, were evaluated as a function of $m_{KOH}$ from the data of Akerlof and Bender[25]. A summary of calculated pH values is given in Table 1.

Table 1. Calculated pH values for various KOH concentrations at 20°C

<table>
<thead>
<tr>
<th>$m_{KOH}$ (mol kg$^{-1}$)</th>
<th>$f_{KOH}$</th>
<th>$a_w$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.96</td>
<td>14.06</td>
</tr>
<tr>
<td>2</td>
<td>0.87</td>
<td>0.92</td>
<td>14.44</td>
</tr>
<tr>
<td>3</td>
<td>1.07</td>
<td>0.87</td>
<td>14.73</td>
</tr>
<tr>
<td>4</td>
<td>1.36</td>
<td>0.82</td>
<td>14.99</td>
</tr>
<tr>
<td>5</td>
<td>1.75</td>
<td>0.76</td>
<td>15.23</td>
</tr>
<tr>
<td>6</td>
<td>2.28</td>
<td>0.69</td>
<td>15.46</td>
</tr>
<tr>
<td>7</td>
<td>2.98</td>
<td>0.63</td>
<td>15.69</td>
</tr>
<tr>
<td>8</td>
<td>3.89</td>
<td>0.56</td>
<td>15.91</td>
</tr>
<tr>
<td>9</td>
<td>5.08</td>
<td>0.50</td>
<td>16.13</td>
</tr>
<tr>
<td>10</td>
<td>6.59</td>
<td>0.44</td>
<td>16.34</td>
</tr>
</tbody>
</table>

The E-pH relation of freshly prepared bismuth electrodes

Figure 1 shows the change of the open circuit potential (OCP) of a freshly prepared Pt/Bi electrode with pH during two consecutive measurements. These data were obtained following the D-method. Similar results were obtained with freshly prepared Pt/Bi/BiO$_x$ electrodes. Both the Pt/Bi and Pt/Bi/BiO$_x$ electrodes gave linear E–pH plots in the high alkaline region (pH 15–16), however, the slope could vary for different electrodes. Usually a slope of $-0.05$ V was found, in some cases a slope of $-0.04$ or $-0.06$ V was found.

The OCP of all of these electrodes was time dependent. This was tested with five Pt/Bi electrodes, placed in KOH solutions of different concentration. The OCP of these electrodes was measured over a period of more than 300 h. Figure 2 shows the E–pH relation at different times. The slope of the E–pH plot alters from $-0.062$ V at the beginning of the experiment to $-0.031$ V after 50 h. After 50 h the slope remains constant, though the OCP still changes.

The E–pH relation of aged Pt/Bi electrodes

An electrode is called aged if it has been in contact with the ageing solution for more than one week (164 h). As can be seen in Fig. 2, the slope and OCP are constant for these electrodes. Figure 3 shows the open circuit potential of a Pt/Bi/aged/2 electrode as a function of molality. These data were obtained following the FH-method. In Fig. 4, these results are replotted as a function of pH. The E–pH plot of the Pt/Bi/aged/2 electrode fits a straight line, with a slope of $-0.046$ V. The results of the Pt/Bi/aged/4 electrode
The change of the $E$–$pH$ relation with time for five Pt/Bi electrodes in solutions of different KOH molality. Numbers in figure indicate time interval.

Fig. 3. Potential of the Pt/Bi/aged/2 electrode as a function of molality: FH-method, from 1 to 10 molal (○) and from 10 to 1 molal (▲).

Fig. 4. Potential of the Pt/Bi/aged/2 (○) and Pt/Bi/aged/4 (△) electrode as a function of pH: FH-method, from 1 to 10 molal.

Fig. 5. Potential of the Pt/Bi/aged/2 electrode as a function of pH: SH-method, starting in the 2 molal KOH solution; curve A. After a 16 h stand in the 6 molal KOH electrolyte, the experiment was continued; curve B. Curve C results from the change of solution from the 10 to the 1 molal electrolyte; (▲) is the electrode potential after a 16 h stand in the two molal electrolyte at the end of the experiment.

Prolonged exposure to a concentrated alkaline solution, on the pH dependence of the Pt/Bi/aged/m electrode. Starting in a 2 molal KOH solution, the potentials were monitored for increasing KOH molality. The electrode potential was recorded up to 6 molal KOH (curve A). After a 16 h stand in this electrolyte the potential had increased with 0.02 V. The measurement of the potential with increasing molality up to 10 molal KOH resulted in curve B. The experiment was continued with the measurement of the potential of this electrode in the one and two molal electrolyte (curve C). Another sixteen hours stand, but now in the 2 molal solution, resulted in almost the same value for the electrode potential as at the beginning of the experiment. Each of the curves A, B and C in Fig. 5: a good linear $E$–$pH$ plot with slopes of respectively $-0.046$, $-0.048$ and $-0.049$ V; however, a shift of about 0.020 V is observed if the measurement is carried out after a 16 h stand in solution. The observed slope and potential at pH 14 for some experiments are summarized in Table 2.

Table 2. The pH dependence of the various types of bismuth electrodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>pH range</th>
<th>Method</th>
<th>Slope (V)</th>
<th>$E$(pH = 14) (V vs sce)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Bi/aged/2</td>
<td>14.1–16.3</td>
<td>FH</td>
<td>$-0.046$</td>
<td>$-0.580$</td>
</tr>
<tr>
<td>Pt/Bi/aged/4</td>
<td>14.5–16.3</td>
<td>FH</td>
<td>$-0.042$</td>
<td>$-0.579$</td>
</tr>
<tr>
<td>Pt/Bi/BiO$_x$</td>
<td>14.8–16.1</td>
<td>FH</td>
<td>$-0.052$</td>
<td>$-0.575$</td>
</tr>
<tr>
<td>Pt/Bi/aged/2</td>
<td>14.5–15.5</td>
<td>SH (A)</td>
<td>$-0.046$</td>
<td>$-0.575$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.5–16.3</td>
<td>(B)</td>
<td>$-0.048$</td>
<td>$-0.558$</td>
</tr>
<tr>
<td></td>
<td>14.1–14.5</td>
<td>(C)</td>
<td>$-0.049$</td>
<td>$-0.584$</td>
</tr>
<tr>
<td>Pt/Bi/aged/6</td>
<td>15.3–16.3</td>
<td>SH (A)</td>
<td>$-0.039$</td>
<td>$-0.569$</td>
</tr>
<tr>
<td></td>
<td>14.8–15.5</td>
<td>(B)</td>
<td>$-0.036$</td>
<td>$-0.593$</td>
</tr>
<tr>
<td>Pt/Bi/aged/8</td>
<td>14.4–15.9</td>
<td>SH (B)</td>
<td>$-0.032$</td>
<td>$-0.594$</td>
</tr>
<tr>
<td>Pt/Bi/aged/10</td>
<td>14.9–16.2</td>
<td>SH (B)</td>
<td>$-0.030$</td>
<td>$-0.593$</td>
</tr>
<tr>
<td>Pt/Bi/BiO$_x$</td>
<td>15.2–16.5</td>
<td>D</td>
<td>$-0.051$</td>
<td>$-0.573$</td>
</tr>
<tr>
<td>Pt/Bi</td>
<td>15.5–16.8</td>
<td>D</td>
<td>$-0.053$</td>
<td>$-0.567$</td>
</tr>
</tbody>
</table>
The morphology and surface composition of the bismuth electrodes

The morphology of the freshly prepared and aged bismuth electrodes was studied with scanning electron microscopy (SEM). The change in morphology of the electrodeposited bismuth plated platinum electrodes on ageing, is presented in Figs 6-10. The characteristic features of freshly deposited bismuth (Fig. 6) change markedly during ageing in 2 molal KOH electrolyte (Figs 7-9). The surface of the electrode becomes partially covered with yellow needles and small "rosette-like" structures. A similar behavior is observed if the electrode is aged in a 6 molal KOH solution; only a smaller number of needles and a larger number of the "rosette-like" structures is observed (Fig. 10).

The X-ray diffraction patterns of freshly prepared Pt/Bi and Pt/Bi/BiO₆ electrodes, showed that the texture of the platinum wire determines the orien-

Fig. 6. Photograph of a freshly prepared Pt/Bi electrode.

Fig. 7. Photograph of a Pt/Bi electrode, aged for 2 days in a 2 molal KOH solution.
tation of the bismuth crystals. This orientation disappeared more and more as the electrode had aged for a longer period of time. The nature of the oxide on the electrode surface could not be identified with this technique.

The ageing process in the 2 and 6 molar solution was also studied with ESCA. Table 3 contains the Bi 4f$_{3/2}$ and 4f$_{1/2}$ binding energy measurements from several aged electrodes and various bismuth compounds.

DISCUSSION

The pH dependence of freshly prepared bismuth electrodes

Freshly prepared Pt/Bi and Pt/Bi/BiO$_2$ electrodes can be used to indicate pH changes in concentrated KOH solutions. The results are reproducible, if these electrodes are in contact with the alkaline solution for a short time (about 15–30 min); on prolonged standing
pH measurement with a Bi electrode

Fig. 10. Photograph of a Pt/Bi electrode, aged for 16 days in a 6 molal KOH solution.

Table 3. Experimental binding energies of various bismuth compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>C 1s</th>
<th>Direct 4f_{5/2}</th>
<th>Corrected* 4f_{5/2}</th>
<th>4f_{7/2}</th>
<th>Corrected* 4f_{7/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
</tr>
<tr>
<td>Pt/Bi</td>
<td>288.4</td>
<td>168.6</td>
<td>163.4</td>
<td>5.2</td>
<td>165.2</td>
</tr>
<tr>
<td>Pt/Bi/aged/2^1</td>
<td>287.2</td>
<td>167.3</td>
<td>162.0</td>
<td>5.3</td>
<td>165.1</td>
</tr>
<tr>
<td>Pt/Bi/aged/2^2</td>
<td>285.8</td>
<td>164.9</td>
<td>159.7</td>
<td>5.2</td>
<td>164.1</td>
</tr>
<tr>
<td>Pt/Bi/aged/6^1</td>
<td>285.7</td>
<td>164.6</td>
<td>159.4</td>
<td>5.2</td>
<td>163.9</td>
</tr>
<tr>
<td>Bi^1</td>
<td>286.3</td>
<td>161.6</td>
<td>156.4</td>
<td>5.3</td>
<td>162.4</td>
</tr>
<tr>
<td>Bi_2O_3^11</td>
<td>287.3</td>
<td>167.2</td>
<td>161.8</td>
<td>5.4</td>
<td>164.9</td>
</tr>
<tr>
<td>Bi_2O_3 · 2H_2O^11</td>
<td>288.0</td>
<td>167.6</td>
<td>162.4</td>
<td>5.2</td>
<td>164.6</td>
</tr>
<tr>
<td>NaBiO_3^11</td>
<td>287.7</td>
<td>167.2</td>
<td>162.0</td>
<td>5.2</td>
<td>164.5</td>
</tr>
</tbody>
</table>

* Measurements referenced to hydrocarbon contaminant C 1s line, assuming a value of 285.0 eV
^1 Aged for 2 days.
^2 Aged for 7 days.
^3 Aged for 16 days.
^11 From [28].

in this solution, a voltage drift is observed (Fig. 2). Therefore, it is necessary to calibrate the electrodes before each experiment.

Both the Pt/Bi and Pt/Bi/BiO_3 electrodes were tested with the D-method (Fig. 1). This method offers a fast technique to measure the response of the electrode potential to pH changes. However, it cannot be used as a calibration procedure, because the temperature of the electrolyte cannot be controlled to 20°C throughout the whole experiment. The heat generated by the dilution of the concentrated alkaline solution causes an increase in temperature. The break from linearity at lower pH values in Fig. 1 can be attributed to this increase in temperature. The D-method offers only information about the behavior of the electrode in an electrolyte of rapidly changing composition.

The pH dependence of aged electrodes

Whereas freshly prepared electrodes are only suited for short time pH measurement, aged electrodes are applicable for several hours. As was shown in Fig. 2 (curves C and D) and 5, the E–pH slope is fairly constant with time for an aged electrode; however, the intercept varies. Therefore, calibration of the electrode prior to use is necessary. Once the slope is determined, the calibration procedure can be restricted to a few measurements.

It was found that the value of the slope of the E–pH plot for the aged electrodes depends on KOH concentration of the ageing electrolyte: the slope was usually less negative for electrodes aged in more concentrated KOH solutions (cf. Table 2, the results of the SH-method).
The potential determining electrode process

If the formation of the bismuth trioxide:

\[ 2Bi + 3H_2O \rightleftharpoons Bi_2O_3 + 6H^+ + 6e^- \]  

(4)
determines the potential of the bismuth electrode in alkaline solutions, as is sometimes assumed\[13, 15]\, then the equation for the electrode potential becomes:

\[ E = E^0_{Bi_2O_3} + CPH + (C/2)\log a_w \]  

(5)

with:

\[ C = -(RT/F)\ln(10) \]

where \( C \) is the "theoretical" slope for the \( E \)–\( pH \) relation; i.e. if the water activity is unity, the electrode potential changes with \( C \) V per \( pH \) unit. The value of \( C \) is \(-0.0582 \) V at \( 20^\circ C \) and \(-0.0592 \) V at \( 25^\circ C \).

Results of the open circuit potential measurements of other authors are reported in Table 4. These data were obtained with freshly prepared electrodeposited bismuth electrodes in buffered solutions of which the alkalinity never exceeded \( pH = 14 \). The slopes of the potential vs \( pH \) plots with stationary bismuth electrodes are generally less negative than the "theoretically" expected value. Measurements with a rotating bismuth electrode of which the surface was cleaned on every rotation, resulted in a nearly "theoretical" slope of \(-0.0562 \) V. A "theoretical" slope was obtained by Sammour et al.\[15\].

The \( E \)–\( pH \) slope and \( E(pH = 14) \) of freshly prepared electrodes obtained in this work for \( pH = 14–16 \), are in reasonable agreement with the findings of other authors. This indicates that the \( pH \) dependence of the potential determining process does not change over a large \( pH \) domain. The slope of aged electrodes is generally less negative, and, therefore, maybe a different electrode process determines the electrode potential. The value of \( E(pH = 14) \) calculated from the thermodynamic data of Pourbaix\[26\] for the formation of bismuth trioxide is \(-0.688 \) V. Latimer\[27\] estimated this value at \(-0.70 \) V vs sce. For the formation of bismuth hydroxide Pourbaix obtained \(-0.581 \) V vs sce at \( 20^\circ C \). The experimental values, listed in Table 2, are close to the latter value, but since the experimental slope differs from the theoretical slope, it is impossible to draw conclusions from this fact.

The deviation of the \( E \)–\( pH \) slope from the "theoretical" value, has been discussed in the literature by several authors. Schwabe\[14\] suggested that the activity of adsorbed hydroxyl ions is less than the activity of bulk hydroxyl ions. From results obtained with freshly prepared bismuth electrodes in alkaline solutions of \( pH \) values < 14, he derived the relation:

\[ \log a_{OH^-} = \text{const.} + 0.88 \log a_{OH^+} \]  

(6)

where the superscripts \( s \) and \( b \) refer to the surface and bulk ion activities, respectively. The value of the \( E \)–\( pH \) slope is then \(-0.051 \) V. If it is assumed that the bismuth oxide at the electrode surface is not in the standard state, or the activity of the oxide is a function of the hydroxyl ion activity, a similar change in slope is obtained. Schwabe also proposed, that the smaller value of the slope could be attributed to the formation of polymeric bismuth oxides:

\[ Bi(n+1)O_2+OH^- \rightleftharpoons Bi_nO_{2n+1}H(n+2) \]  

(7)

However, this is not likely, since in concentrated alkaline solutions these ionic bismuth oxide compounds do not exist.

Although the former suggestions are quite reasonable explanations for the smaller value of the slope, in concentrated alkaline solutions, two other aspects play an important role. Firstly, the water activity deviates from unity and secondly, bismuth oxide compounds become slightly soluble. The impact of the changing water activity with changing electrolyte composition is easily demonstrated with the Nernst equation. If the formation of \( Bi(OH)_3 \) is taken to be the potential determining process, the \( E \)–\( pH \) relation is:

\[ E = E^0_{Bi(OH)_3} + CPH + C\log a_w \]  

(8)

A plot of the potential vs \( pH \) calculated according to Equation (5) or (8) is not linear for strong alkaline solutions, because \( C \) does not change linearly with \( pH \) (cf. Table 1). Taking this into account, the slope of the \( E \)–\( pH \) curve according to Equation (5) alters from \(-0.058 \) V for \( pH \) values up to \( pH = 13 \), to approximately \(-0.051 \) V for \( pH = 16 \), while the formation of the bismuth hydroxide yields a slope of \(-0.045 \) V at \( pH = 16 \).

From the morphological study of various bismuth electrodes it is not clear which oxide is present at the surface of the electrode, though the yellow crystals (Fig. 8) indicate \( Bi_2O_3 \). In fact, the presence of these yellow needles gives the impression that bismuth dissolves in the electrolyte and is redeposited as trioxide on the electrode. If the dissolution of bismuth:

\[ Bi + 2H_2O \rightleftharpoons BiO_2 + 4H^+ + 3e^- \]  

(9)
pH measurement with a Bi electrode

is the potential determining process. The slope for the $E$–$pH$ plot is $-0.077$ V. This reaction can of course be written as two consecutive steps; first the oxidation of the metal according to Equation (4), which is the potential determining process, followed by the dissolution of the oxide: then a slope of $-0.058$ V is expected. If Equation (9) occurs at a freshly prepared electrode then, on ageing, the following reactions can take place:

$$
2\text{BiO}_2^- + 2\text{H}^+ \rightleftharpoons \text{Bi}_2\text{O}_3 + \text{H}_2\text{O}, \quad (10)
$$

$$
4\text{BiO}_2^- + 2\text{H}^+ \rightleftharpoons \text{Bi}_4\text{O}_7 + \text{H}_2\text{O} + 2e^-, \quad (11)
$$

$$
2\text{BiO}_2^- \rightleftharpoons \text{Bi}_2\text{O}_4 + 2e^-, \quad (12)
$$

$$
2\text{BiO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{Bi}_2\text{O}_3 + 2\text{H}^+ + 4e^- \quad (13)
$$

The $E$–$pH$ slopes of the electrochemical reactions (Equations (11)–(13)) are $+0.058$, 0 and $-0.029$ V respectively.

To investigate, which oxides are present at the electrode surface, we studied the surface composition of aged electrodes with ESCA. However, from these results (Table 3) it is impossible to obtain conclusive evidence, as to which bismuth oxide species is predominantly present at the electrode surface. Though, on ageing, a change in electrode surface composition is observed, it is not possible to ascribe this change to the conversion of one bismuth oxide to another. Also, a serious drawback of the ESCA technique is that very high vacuum is needed, which can inflict a considerable change in surface composition.

The results of Table 2 show that only for a freshly prepared Pt/Bi or Pt/Bi/BiO$_2$ electrode the $E$–$pH$ slope is close to the Nernstian slope. The lower value of the slope can be attributed to the non-linear relation of $\log a_w$ and pH in concentrated alkaline solutions. So here the bismuth electrode behaves as a type I electrode. For all aged electrodes the absolute value of the $E$–$pH$ slope decreases with increasing KOH concentration. This could indicate that either Equation (13) becomes potential determining or that hydroxyl ion exchange and adsorption processes play a role such as Equations (7) and (6), respectively. Moreover, bismuth oxide compounds are definitely present at the electrode surface and maybe even in solution, so a type II electrode behavior seems likely.

REFERENCES