Monatshefte für Chemie 135, 1475–1488 (2004)
DOI 10.1007/s00706-004-0239-x

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Comparison of Several Calibration Procedures for Glass Electrodes in Proton Concentration

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Received March 31, 2004; accepted (revised) June 22, 2004

Summary. Several reported procedures for calibrating glass electrodes in proton concentration are compared. Some recommendations for non-experts are also given. The examined procedures can be classified into two broad categories, namely: those based on direct potential difference measurements of solutions of known proton concentration and those that use one or several *pH* standards to calibrate the electrode and subsequently measure the *pH* of solutions containing known proton concentrations. With a single buffer, the two types of procedures lead to equivalent results. However, if two *pH* buffers are used, the slope of the calibration graph in proton concentration will differ from the real electrode slope to an extent proportional to the difference between the liquid junction potentials of the two buffers. Therefore, any other method is preferable under these circumstances.

Keywords. Glass electrode; Proton concentration; Electrode response; Potentiometry; Calibration.

Introduction

Glass electrode calibration in proton activity has been widely studied in bibliography [1]. Although the potential measured follows a linear relationship with the logarithm of the activity of proton, the experimental slope obtained usually departs from the *Nernst*ian value. Owing to this fact, a bracketing procedure has been recommended in *pH* determinations for many years. In the bracketing procedure two different *pH* standards are used, so formal potential and slope of electrode are determined. *pH*-meters using this procedure have been developed and they are commonly used in laboratories. A straight line is calculated in the calibration with the two buffers and the *pH* of the unknown solution is calculated assuming linearity between *pH* and potential. If non-*Nernst*ian slope response is accepted in *pH*

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measurements, this fact should also be taken into account when calibration of electrode is done in proton concentration. The aim of this paper is to classify and compare the different procedures followed in measurements of proton concentration and to analyse the effect of the deviation from *Nernst*ian response on these measurements.

The ability to quantify the concentration of the proton, or any other species to which an electrode may respond, from potential difference or *pX* measurements of a solution has obvious analytical interest. At the same time, one of the main applications of calibration in proton concentration is the determination of stoichiometric equilibrium constants in saline media. For example, our research group, among others, has been devoted to this subject during several years [2–10]. Therefore, owing to the great significance of the calibration in proton concentration on *pK* determinations, we have decided to carry out a detailed analysis in this topic.

Equilibrium constants can be defined in terms of concentrations, *viz. stoichiometric constants*, activities, *viz. thermodynamic constants*, and combinations of activities and concentrations, *viz. mixed constants* [11]. A number of reported acidity constants of the last type has been determined by using a glass electrode to measure *pH* and various analytical methods to quantify the concentrations of the other species in solution. However, as noted by *McBryde* [11], many constants calculated in this way, lack of physical significance since the electrode was calibrated with dilute solutions, whereas the constants were determined in solutions of high ionic strength. The two types of solutions used can be expected to differ in activity coefficients and liquid junction potentials. As pointed out by *Irving et al.* [12], one cannot expect that the measured *pH* obtained under these conditions will coincide with $-\lg a_{\mathrm{H}^+}$.

The determination of stoichiometric constants appears to be of greater use. The extrapolation of stoichiometric constants to zero ionic strength allows the estimation of thermodynamic constants. Although the glass electrode responds to proton activity, the proton concentration, $[\mathrm{H}^+]$, can also be determined provided that the electrode is previously calibrated. In media of constant ionic strength, the proton activity coefficient is constant. Thus the potential difference measured between indicator and reference electrode can be directly related to the logarithm of the proton concentration. This is possible if we are working in a saline medium where concentration of acids and bases are small compared with the salt concentration, so activity coefficient and liquid junction potential can be considered constant, *i.e.* we apply the ionic medium method which according to *Sillén* [13] was proposed by *G. Bodländer* around 1904.

Therefore, potentiometry with glass electrodes is an invaluable, widely used method for the determination of equilibrium constants [14]. The prior calibration [15] of the electrode is one of the most influential steps in the determination of such constants. This paper compiles available evidence on the several reported procedures for calibration of glass electrodes and compares their performance.

Results and Discussion

Calibration of a Glass Electrode. Calibration Methods

Ion-selective electrodes, which include the glass electrode, can be calibrated following IUPAC's recommendations [16], using solutions of known activity or concentration. However, using a solution of known activity for a given ion is strictly impossible as it entails knowing the activity coefficient of a single ion, which must be assigned on the basis of non-thermodynamic assumptions made in establishing the *pH* scale. Solutions of known concentration are easier to obtain, since there is no need to estimate the activity of individual ions.

When the proton concentration of a solution is determined by using a glass electrode, one will sooner or later have to use solutions of known [H^+]; whether or not solutions of known *pH* will also have to be employed is not so obvious. In fact, authors use different approaches to this problem. According to these approaches, calibration methods can be classified into two large groups, namely: (a) Those where the electrode is directly calibrated by using solutions of known proton concentration. From the calibration straight line, potential difference measurements of an unknown solution can be directly related with its proton concentration. (b) Those where the electrode is first calibrated with one or more buffers and then it is used to measure the *pH* of solutions of known [H^+].

Calibration with Solutions of Known Proton Concentration

Methods based on this principle have the advantage that they avoid the use of the *pH* scale [16, 17].

As a rule, the system consisting of the working solution and the glass electrode can be schematized as follows [18]

$$\text{external ref. elect., KCl(sat)} \vdots \text{solution} \,|\text{glass membrane}\,|\text{internal ref. elect.}$$

where $\vdots$ denotes the liquid junction.

The measured potential difference comprises several contributions. Two of them are due to the reference electrodes, of opposite sign and, usually, comparable magnitude, and have a constant value, denoted by E_r in this paper. There are also two potential differences due to the liquid junction and the glass membrane which are designated as E_j and E_v, respectively; thus, following *May* [17], the overall potential difference for the electrochemical cell can be expressed as shown in Eq. (1).

$$E = E_r + E_j + E_v \tag{1}$$

Since the glass electrode exhibits a *Nernst*ian response, the previous equation can be rewritten as Eq. (2), where s denotes the *Nernst*ian slope (59.16 mV at 25°C), E_{as} the asymmetry potential, $a_{H^+_{int}}$ the proton activity of the inner solution of the glass electrode, and a_{H^+} is the proton activity of the solution in which the electrode is immersed.

$$\begin{aligned} E &= E_r + E_j + E_{as} + s \lg \frac{a_{H^+}}{a_{H^+_{int}}} \\ E &= E^0 + E_j + s \lg a_{H^+} \quad \text{where } E^0 = E_r + E_{as} - s \lg a_{H^+_{int}} \end{aligned} \tag{2}$$

If the ionic strength is constant, so will be the logarithm of the activity coefficient, $\lg y_{H^+}$, what leads to Eqs. (3) and (4).

$$E = E_{const}(I) + s \lg [H^+] \tag{3}$$

where

$$E_{\text{const}}(I) = E^0 + E_\text{j} + s \lg y_{\text{H}^+} \tag{4}$$

The purpose of the calibration process is to determine s and E_{const} in Eq. (3). In this way, the proton concentration of any solution can be determined by measuring its potential difference and solving the equation for [H$^+$]. Potential differences of several solutions with known proton concentration have to be measured in order to obtain s and E_{const}. If the ionic strength is kept constant by addition of an excess of an inert electrolyte, both liquid junction potential and activity coefficient of the proton remain constant and the value of E_{const} can be determined at the desired ionic strength. Of course, proton concentration has to be varied, but if proton concentration is small compared to the concentration of the inert electrolyte, all parameters encompassed in E_{const} will remain constant, unless very acidic or basic solutions are used.

One usual way to calibrate the glass electrode is by addition of a base to an acid, both of known concentrations, at a fixed ionic strength. One must use an alkali or acid excess to ensure that measurements will be made in a buffered region; otherwise, small errors in the concentrations can lead to utterly spurious results. However, solutions too acidic raise the liquid junction potential whereas too alkaline ones give rise to the so called "alkali error". *May et al.* [17] recommend the following concentration ranges (as −lg [H$^+$]) to calibrate glass electrodes: 2.3–2.9 in acidic media and 10.8–11.3 in basic ones.

When a strong base is added to a strong acid, both of known concentration, [H$^+$] prior to the equivalence point, and [OH$^-$] beyond it, will be given by Eq. (5), where c_a and c_b are the acid and base concentrations, respectively, V_0 the initial acid volume, and v the added base volume.

$$[\text{H}^+] = \frac{c_\text{a} V_0 - c_b v}{V_0 + v} \qquad [\text{OH}^-] = \frac{c_\text{b} v - c_\text{a} V_0}{V_0 + v} \tag{5}$$

However, the electrode is sensitive to the proton concentration, which is related to the hydroxyl ion concentration *via* the ionic product of water, K_w^*. Therefore, after the equivalence point, Eq. (6) is obtained.

$$[\text{H}^+] = \frac{K_\text{w}^*}{[\text{OH}^-]} = \frac{K_\text{w}^* \cdot (V_0 + v)}{(c_\text{b} v - c_\text{a} V_0)} \tag{6}$$

Substitution of the expression for the proton concentration prior to the equivalence point into Eq. (3) yields Eq. (7) and after the equivalence point Eq. (8).

$$E = E_{\text{const}}(I) + s \ \lg \frac{c_\text{a} V_0 - c_\text{b} v}{V_0 + v} \tag{7}$$

$$E = E_{\text{const}}(I) + s \ \lg \frac{K_\text{w}^* \cdot (V_0 + v)}{(c_\text{b} v - c_\text{a} V_0)} = E_{\text{const}}(I) + s \ \lg K_\text{w}^* + s \ \lg \frac{(V_0 + v)}{(c_\text{b} v - c_\text{a} V_0)} \tag{8}$$

A plot of E against the logarithmic functions in Eqs. (7) and (8) usually leads to s values departing from 59.16 mV at 25°C, both in acidic and in basic media [19]. Any systematic error in the acid or base concentration will affect the value of the slope obtained by fitting experimental data to Eqs. (7) and (8).

Calibration can be done, as well, by adding volumes v of a strong acid with concentration c_a to a volume V_0 of an inert electrolyte solution, and using Eq. (9).

$$E = E_{\mathrm{const}}(I) + s \lg [\mathrm{H}^+] = E_{\mathrm{const}}(I) + s \lg \frac{c_a \cdot v}{V_0 + v}$$

$$E = [E_{\mathrm{const}}(I) + s \lg c_a] + s \lg \frac{v}{V_0 + v} \tag{9}$$

Similarly, when a strong base of concentration c_b is added to an inert electrolyte solution, Eq. (10) can be used.

$$E = E_{\mathrm{const}}(I) + s \lg [\mathrm{H}^+] = E_{\mathrm{const}}(I) + s \lg \frac{(V_0 + v) \cdot K_w^*}{c_b \cdot v}$$

$$E = \left[E_{\mathrm{const}}(I) + s \lg \frac{K_w^*}{c_b}\right] + s \lg \frac{V_0 + v}{v} \tag{10}$$

With the second method, a systematic error in the acid or base concentration will have no effect on the slopes of Eqs. (9) and (10) as they will only be included in the intercept.

Fiol et al. [19] concluded that systematic errors in the concentrations have different effects on the electrode response depending on the specific form of the calibration equation. If an acid or base is added to the inert electrolyte solution, it will be determined to what extent the electrode used exhibits a *Nernst*ian behaviour. For this very reason, however, the method will be insensitive to systematic errors in the concentrations.

Figure 1 shows calibration lines obtained with a single glass electrode (electrode ***a***, see Experimental), using a Ag/AgCl electrode as reference electrode dipped in the working solution. Therefore, with this setting, there was no liquid junction present. Ionic strength was kept constant at $I = 0.4\,M$, by addition of

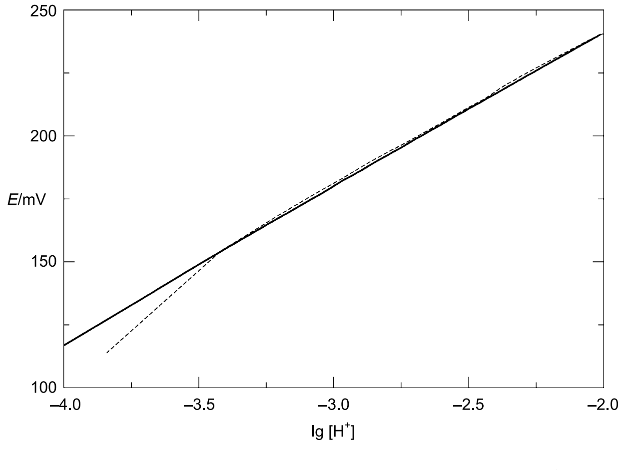

Fig. 1. Calibration lines obtained with a single glass electrode and a Ag/AgCl reference electrode, $I = 0.4\,M$ (KCl); solid line corresponds to a calibration where a strong acid was added to a solution of the inert electrolyte whereas dashed line corresponds to the acid region of a strong acid-strong base titration

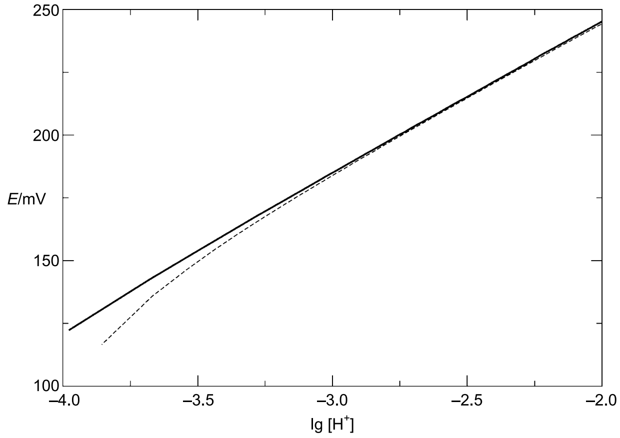

Fig. 2. Calibration lines obtained with a combination glass electrode; solid line corresponds to a calibration where a strong acid was added to a solution of the inert electrolyte whereas dashed line corresponds to the acid region of a strong acid-strong base titration

KCl. Solid lines correspond to calibrations where a strong acid was added to a solution of the inert electrolyte whereas dashed lines correspond to the acidic region of a strong acid-strong base titration. Figure 2 shows similar calibrations made with a combination glass electrode (electrode ***b***, see Experimental), therefore a liquid junction was present in these calibrations. Both figures show that the acid-base calibrations are curved lines, whilst acid-inert electrolyte calibrations are straight lines. Since calibrations have been made in systems with and without liquid junction, the curvature observed in the calibration lines seems to be related to the experimental procedure employed and not to a variation in the liquid junction potential. These figures show that curvature appears owing to the combination of errors in the concentrations even when there is no liquid junction in the cell. Thus, to check the response of the electrode it will be more sensible to make a strong acid over electrolyte calibration instead of using a strong acid-strong base titration. Examples of this procedure can be found in bibliography. *Fiol et al.* [19] and *Baumann* [20] used the same method at high salt concentrations to examine the behaviour of glass electrodes over broader proton concentration ranges than those recommended by *May* [17]. *McBryde* [11] also noted the suitability of this procedure for calibrating glass electrodes, even though he did not use it himself.

Experimental potentiometric data from strong acid-strong base titration can also be analysed following a different procedure. Instead of using Eqs. (7) and (8), other fitting functions, proposed by *Gran* [21–23] can be used. With these fitting functions, equivalence point, V_{eq}, can also be determined. We know that $c_a V_0 = c_b V_{eq}$. Substitution of $c_a V_0$ by $c_b V_{eq}$ in Eq. (7) and subsequent rearrangement yields Eq. (11), where $\psi = (V_0 + v)10^{E/s}$ is known as *Gran* function.

$$\psi = (V_0 + v)10^{E/s} = c_b(V_{eq} - v)10^{E_{const}/s} \qquad (11)$$

A plot of ψ *vs.* v represents a straight line that intercepts the x-axis at $v = V_{eq}$. To calculate ψ, electrode slope is required. From the fitting estimates, the electrode formal potential can also be determined. Following a similar substitution in Eq. (8), Eq. (12) can be obtained.

$$\psi' = (V_0 + v)10^{-E/s} = \frac{c_b}{K_w^*}(v - V_{eq})10^{-E_{const}/s} \tag{12}$$

A plot of ψ', the *Gran* function for basic media, *vs.* v yields a second straight line, which intercepts the x-axis at the same point as the function ψ, *i.e.* $v = V_{eq}$. However, the presence of carbonate in the strong basic solution makes the second line to curve close to the equivalence point. This fact allows not only the identification of carbonate in the solution, but also its quantification, see Ref. [24].

On the other hand, *May et al.* [17] found an alternative solution to the problem posed by errors in the concentrations involved in acid-base titrations. They developed the software MAGEC, in which the concentration of titrated substances is slightly altered until the slope reaches the *Nernst*ian value.

One very important factor on the calibration in the alkaline region is the ionic product of water, K_w, which must be known in order to convert $[H^+]$ into $[OH^-]$. Consequently, any error in K_w will introduce uncertainty in the alkali concentration. In fact, only one of these parameters (c_b or K_w) can be determined by using the procedure proposed by May *et al.* [17]. If the calibration is done by adding a base to the inert electrolyte, the experimentalist should be aware of the alkaline error on the glass electrode [25–27]. As noted by *Vasconcellos et al.* [28], this fact makes the determination of pK_w even more difficult.

One of the criticisms that the above-described procedure has received is the narrow $p[H^+]$ ranges over which calibration is possible, which entails extrapolation of the parameter values obtained at proton concentrations where the liquid junction potential might be different [29]. Although May *et al.* [17] had pointed out that extrapolations to other $p[H^+]$ ranges were inadvisable, they also had noted the difficulty in quantifying the errors arising from changes in the liquid junction potential [30]. In Ref. [31] combination glass electrodes have been used to determine the equilibrium constants of mono-, di-, and trimethylamine in KCl at $I = 0.2\,M$. Calibration was done in an acidic medium, $p[H^+] = 2$–3 and a good *Nernst*ian response was found. The agreement between the pK^* values with those calculated by *Everett* [32], who used a hydrogen electrode, is excellent with differences in some cases of a few thousandths of pK units. So extrapolation does not seem to be a severe problem in the procedure.

Another approach to the calibration involves using weak acids and bases. Provided that their dissociation constants under the specific working conditions are known, $[H^+]$ can be determined, even though the process is mathematically more complex than with strong acids and bases [33, 34]. One shortcoming of this procedure is that it requires the knowledge of the dissociation constants involved with acceptable precision. However, the situation is usually the opposite, *i.e.* the electrode is calibrated first and the constants are determined afterward. In any case, the quality of reported constant values is difficult to assess [28]. In fact, one of the factors introducing especially severe errors in equilibrium constants is an incorrect calibration of the electrode in addition to errors in the analytical concentrations of the reactants and in the allegedly known constants [35]. One interesting approach to overcome this hindrance is to perform an *internal calibration*, *i.e.* the same computational program used to refine the constants is employed to optimise the calibration parameters [17, 36].

The preceding discussion refers to the determination of the calibration parameters for an electrolyte at a given ionic strength. However, because equilibrium constants are usually determined as a function of ionic strength, it would be interesting to examine the variation of the formal potential with I [37]. *Brandariz et al.* [7, 15] used glass electrodes to determine the variation of E_{const} with I for several electrolytes and studied the dependence E_{const} (I) by means of *Pitzer* model to deal with the activity coefficients. This model can be used to standardise *pH* buffers at high ionic strength as it was done in Ref. [10].

Calibration with Solutions of Known pH

Some authors use the glass electrode calibrated with one or more buffers of known proton activity and *pH* values obtained with a *pH*-meter rather than measuring potential difference values. These methods can be classified into two broad categories, namely: (a) Those that use a single buffer for calibration and where the *pH* values obtained with the potentiometer do not coincide with $-\lg a_{\mathrm{H}^+}$ of the solution. (b) Those that use several buffers.

When the electrode is standardised with a standard buffer of known *pH* (S), the relationship between the potential difference value read by the potentiometer, E, and the buffer *pH*, is given by Eq. (13) [12], where E_{j} denotes the liquid junction potential between the buffer and the solution in the external reference electrode.

$$pH(\mathrm{S}) = \frac{-E + E^0 + E_{\mathrm{j}}}{s} \tag{13}$$

If the same electrode system is used to measure potential difference, E', for any other solution, then the pH' value read by the potentiometer will be given by Eq. (14) [1, 34].

$$pH' = pH(\mathrm{S}) - \frac{(E' - E) - (E'_{\mathrm{j}} - E_{\mathrm{j}})}{s} \tag{14}$$

The value measured by the *pH*-meter, pH', does not coincide with $-\lg a_{\mathrm{H}^+}$ unless the difference between the liquid junction potentials is zero, which is rarely the case.

The relationship between the proton concentration and the measured *pH*, as it will be shown later on, can be expressed by Eq. (15), where A is a constant for a certain ionic strength and is obtained by measuring *pH* in solutions of known proton concentration.

$$pH = p[\mathrm{H}^+] + A \tag{15}$$

Even though *pH* is not the true proton activity, Eq. (15) is quite valid for calibration as the difference between the liquid junction potentials and the activity coefficient for the proton in the ionic medium used are both encompassed by the constant A. The proton concentration $[\mathrm{H}^+]$ of an unknown solution can be calculated by substitution of the A value into Eq. (15) and measuring *pH* for the solution following the same experimental conditions as for calibration, *i.e.* by using the same buffer and ionic strength as in the solution of known proton concentration [12]. As regards to the standard in proton concentration, the same two approaches can be adopted, as in the previous section, namely: (a) Titrating a strong acid with a strong base, both of known concentration and adjusted ionic strength. In this way, $[H^+]$ will be known at each titration point and *pH* will be measured after each addition. This procedure is used by *Irving et al.* [12]. *Gran* method can be used to deal with the experimental data as it is shown in Refs. [21–23]. According to *Fiol et al.* [19], however, the acid or base can also be added to water to have the same effect. (b) Titrating a weak acid or base with one or even more dissociation constants, the values of which are known with enough accuracy. From the charge and mass balance equations, and those for the equilibrium constants, $[H^+]$ can be obtained at each titration point. However, this procedure entails solving a polynomial function of $[H^+]$ of variable order depending on the number of dissociation groups of the substance used. One typical example was reported by *Hedwig et al.* [34]. The chief advantage of this method is that it allows the calibration equation to be validated over a broad *pH* range. However, it requires the precise knowledge of the dissociation constants of the substance.

Of course, another way of canceling the liquid junction potentials of Eq. (14) is by adjusting the ionic strength of the solutions used. The imbalances resulting from ionic strength differences between the calibration standards and the unknown solutions can be offset by using buffers of adjusted ionic strength. However, this is not easy to achieve (*e.g.* NIST buffers exhibit different ionic strengths). *Vasconcellos et al.* [28] estimated *pH* and $p[H^+]$ for three buffers with the same ionic strength and obtained a calibration curve of three points at $I = 0.1\,M$. This method has the disadvantage that it entails knowing the activity of the buffers to which the inert electrolyte is added in order to obtain the desired ionic strength.

Comparison of Calibration Methods

Let us begin by comparing the methods that use one *pH* buffer and subsequently compare these with the methods that make direct potential difference measurements. According to *Nancollas et al.* [38], the slope of the glass electrode is usually slightly smaller than the *Nernst*ian value (59.16 mV at 25°C) [39, 40]. They considered slope values between 58.6 and 59.16 mV at 25°C acceptable for an electrode. Figure 3 shows, as an example, the slopes of three different electrodes at

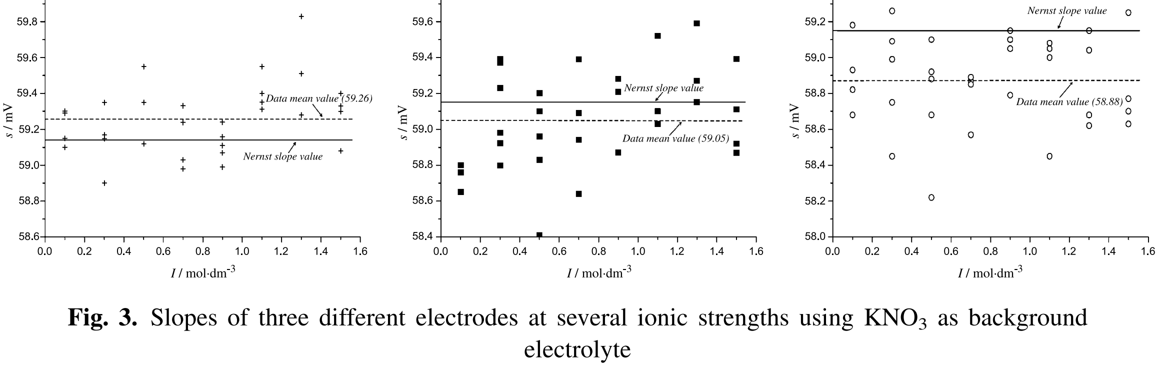

Fig. 3. Slopes of three different electrodes at several ionic strengths using KNO_3 as background electrolyte

several ionic strengths using KNO_3 as background electrolyte. One of them exhibits a smaller slope than the theoretical value, another one higher, whereas in the third one the slope values obtained are distributed around the *Nernst* value. This is the experimental behaviour which is usually found for a glass electrode, that is, *Nernst*ian and sometimes with small deviations. In these situations Eq. (3) is still correct when the experimental value obtained for the slope is used rather than the theoretical one. For this reason, we will study the situation in the presence of an electrode operating with a slope s' instead of s.

When the potentiometer is calibrated with a single buffer, the *pH*-meter measures the corresponding potential difference, E_1, and a value of pH_1 is assigned to this solution. The instrument calibration equation will be that of an *E-pH* plot with the following properties: (a) The slope will coincide with the *Nernst*ian slope, s, even if the real slope of the electrode is s'. (b) The line will pass through the point (pH_1, E_1), or, based on Eq. (2), through (pH_1, $E^0 + E_{j1} - s'\, pH_1$).

The equation of the straight line will then be given by Eq. (16).

$$E = [E^0 + E_{j1} - pH_1(s' - s)] - s\, pH \tag{16}$$

Consequently, the *pH*-meter reading for a generic solution denoted by subscript 3 will be described by Eq. (17).

$$pH_3 = \frac{[E^0 + E_{j1} - pH_1(s' - s)] - E_3}{s} \tag{17}$$

However, based on Eq. (2), the $-\lg a_{H_3^+}$ value of the solution will be as shown in Eq. (18).

$$-\lg a_{H_3^+} = \frac{-E_3 + E^0 + E_{j3}}{s'} \tag{18}$$

Equaling E_3 from Eqs. (17) and (18), and substitution of $-\lg a_{H_3^+}$ by $p[H^+] - \lg y_{H^+}$ yields Eq. (19).

$$-\lg a_{H_3^+} = -\lg y_{H_3^+} + p[H^+]_3 = \frac{E_{j3} - E_{j1}}{s'} + pH_1 \frac{s' - s}{s'} + \frac{s}{s'}\, pH_3$$

$$p[H^+]_3 = C + \frac{s}{s'}\, pH_3 \text{ where } C = \left[\lg y_{H_3^+} - \left(\frac{E_{j1} - E_{j3} - pH_1(s' - s)}{s'}\right)\right] \tag{19}$$

Equation (19) clearly shows that *pH* and $-\lg a_{H_3^+}$ coincide when the difference between the liquid junction potentials is zero ($E_{j1} = E_{j3}$) and the real slope of the electrode is used ($s' = s$). If we measure the *pH* of several solutions of known proton concentration, a linear fit yields C and s/s'. The intercept, C, is a combination of constants and it only depends on the ionic strength and buffer used. Also, the deviation from unity of the slope of the fitted curve is a measure of the deviation from the *Nernst*ian behaviour (within the range of experimental error). When the electrode is calibrated by measuring E and using Eq. (3), the slope for the electrode is obtained directly. For example, if s' at 25°C is found to be 58.6 mV, then a plot of *pH vs.* $p[H^+]$ obtained by calibrating with the same electrode and a single buffer will have a slope of 1.0096.

Consequently, the two types of method for calibrating a glass electrode, *viz.* those based on measurements of E against $p[\mathrm{H}^+]$, and pH against $p[\mathrm{H}^+]$ (with one buffer calibration), provide essentially identical results. In both cases, the intercept of the plot is related to $\lg y_{\mathrm{H}^+}$ and depends on the ionic strength and also on the buffer in the latter procedure, whereas the slope of the fitted line coincides with the slope s' for the electrode in the former case and is the ratio of the theoretical to the experimental value in the latter. Obviously, one should bear in mind that, as shown earlier, errors in the concentrations used during the titration of a strong acid with a strong base or *vice versa* affect the slope of the fitted line.

The situation is different when the pH-meter is calibrated with two buffers, as it is usually the case in the determination of proton activities. The internal calibration line used by the potentiometer will be one passing through the following two points: $(pH_1, E^0 + E_{\mathrm{j}1} - s'\, pH_1), (pH_2, E^0 + E_{\mathrm{j}2} - s'\, pH_2)$. The equation for the internal calibration line of the instrument will then be as shown in Eq. (20).

$$E = \left(E^0 + E_{\mathrm{j}1} - \frac{E_{\mathrm{j}2} - E_{\mathrm{j}1}}{pH_2 - pH_1} pH_1\right) - \left(s' - \frac{E_{\mathrm{j}2} - E_{\mathrm{j}1}}{pH_2 - pH_1}\right) \cdot\ pH \tag{20}$$

If the electrode is immersed, at this point, in a third solution with an ionic strength different from those of the two buffers, then the potential measured by the instrument will be related to $-\lg a_{\mathrm{H}_3^+}$ of the solution via Eq. (18) and through the measured pH (Eq. (20)). Equaling the potential, rearranging, and substituting pH by $p[\mathrm{H}^+]$ and the activity coefficient yields Eq. (21).

$$\begin{aligned} p[H^+]_3 &= C' + \left(1 - \frac{E_{\mathrm{j}2} - E_{\mathrm{j}1}}{(pH_2 - pH_1)s'}\right) pH_3 \\ \text{where} \quad C' &= \lg y_{\mathrm{H}_3^+} + pH_1 \frac{E_{\mathrm{j}2} - E_{\mathrm{j}1}}{(pH_2 - pH_1)s'} + \frac{E_{\mathrm{j}3} - E_{\mathrm{j}1}}{s'} \end{aligned} \tag{21}$$

It should be noted that, although the expression for C' is relatively complex, it is just a sum of constants. It can also be seen that the slope deviates from unity owing to the difference between the liquid junction potentials. This conclusion is reached even in the presence of a strictly *Nernst*ian behaviour, $s = s'$. One might think that, even if the buffers have a different ionic strength, the difference between the liquid junction potentials cannot be so large as to pose any problem. In any case, the systematic error thus introduced will be difficult to assess.

When the calibration is performed by adding acid to water (or an acid to base) we obtain a large number of pairs ($-\lg[\mathrm{H}^+]$, potential) or ($-\lg[\mathrm{H}^+]$, *pH*) and a linear regression yields E_{const} and s' (the real value of the electrode slope), so this has to be considered a multi-point calibration method. A different question is whether prior to this calibration, the use of two standard buffers is necessary or not (when pH is measured). When pH is the desired quantity, the bracketing procedure or the multi-point calibration with standard buffers is recommended in order to assess the value of the electrode slope, even if residual liquid junction potentials are present. But if we want to measure proton concentration, then the use of two buffers introduces the residual liquid junction potential in the calibration equations. This is unavoidable when pH is the desired quantity, but not when $p[\mathrm{H}^+]$ is required, because the multi-point calibration is performed with a solution of known proton concentration. In fact, when a concentration is to be measured the use of *pH* standards in activity is not necessary [41].

Conclusions

Reported procedures for calibrating glass electrodes in proton concentration with a view to determine stoichiometric equilibrium constants are compared. The procedures are classified into two broad groups, namely: those based on direct measurements of E against lg $[\mathrm{H}^+]$ and those were the electrode is calibrated with one or several *pH* buffers and the *pH* of solutions of known proton concentration is measured. The two types of methods were found to give identical results when a single buffer is used. However, if two buffers are used, the slope of the calibration in proton concentration will differ from that for the electrode, the deviation arising from the difference between the liquid junction potential of the two buffers. Even more, the use of two buffers provides no additional advantage in the estimation of $[\mathrm{H}^+]$. Therefore, a direct measurement of the potential difference is recommended or a *pH* measurement, but only when a single standard is used to calibrate the electrode.

Measurements of potential difference or *pH* of known proton concentration solutions can be performed in several ways: (a) Adding an acid to a solution of inert electrolyte, and subsequently, the *pH* or potential difference is measured. (b) Doing a potentiometric titration of a strong acid with a strong base. (c) Doing a potentiometric titration of a weak acid with a strong base or *vice versa*.

Each option has its pros and cons. Our research group has usually followed the first option. The main advantage is that it allows to check the electrode performance and also to calculate the slope, s', from a representation of E *vs.* lg $[\mathrm{H}^+]$ (see Eq. (3)). The slope should be close to the *Nernst* slope, s. If $p[\mathrm{H}^+]$ *vs.* *pH* is plotted, the straight line obtained has a slope equal to s/s', so both procedures are equivalent and both provide the same information. The main disadvantage of the method is that the calibration is done in an acidic medium and the calibration equation is usually employed in a totally different $p[\mathrm{H}^+]$ range. To avoid subsequently problems, special care must be taken into account when the slope of the E *vs.* $p[\mathrm{H}^+]$ function is determined.

Other researchers have used strong acid-base titrations to calibrate the electrode. To the authors' opinion, this method does not provide any further advantage compared to the previous method. An additional disadvantage of this second method is that small errors in the concentrations give rise to curvatures in the E *vs.* lg $[\mathrm{H}^+]$ plots and the electrode slope differs from the *Nernst*ian value which are the phenomena observed for electrodes that show a poor response. This effect is not observed in the first mentioned method, which is insensitive to errors in concentrations.

In the third method using weak acids or bases, the calculation of proton concentrations is more complex from a mathematical point of view. However, nowadays, calculation programs make this work easy. In this case, a severe problem is not only the accuracy of the substances' concentrations, but the accuracy of the equilibrium constants as well. The only advantage of this third method is that the careful selection of the acid (or base) allows to calibrate the electrode in a very specific $p[H^+]$ range. Thus this method is recommended in special situations, such as, for example, $p[H^+]$ measurements in seawater. *Millero* recommends the use of standards prepared in artificial seawater to calibrate the electrode. A substance with a pK around 8 can be used in a solution of several salts that simulate seawater composition. Some possible substances to use are recommended in Ref. [43].

Experimental

Calibrations were performed in two ways: (a) Variable volumes of a strong acid were successively added to an initial volume of inert electrolyte solution. A detailed description of the method can be found in Ref. [15]. (b) Variable volumes of a strong base were successively added to an initial volume of a strong acid solution. We carried out experiments at an ionic strength, $I = 0.4\,M$, adjusted with KCl. All reagents (HNO_3, KOH, KCl) were Merck p.a. The water used to prepare the solutions was purified by passage through a Millipore Milli-Q system. Solutions were standardised as it follows. A stock solution of KOH was standardised with potassium hydrogen phthalate (Carlo Erba, PRE) using phenolphthalein to determine the equivalence point. Once the KOH concentration was accurately measured this solution was used to determine the concentration of the HNO_3 stock solution using also phenolphthalein as indicator. Working solutions for titrations were prepared by dilution of the stock solutions, adding the required amount of KCl to adjust the ionic strength. Special care must be taken for the accurate determination of acid and base concentrations since the first calibration method will not show any effect in case of using erroneous concentrations.

All experiments were performed in a dual-wall cell thermostated with water at $25.0 \pm 0.1°C$. Nitrogen of 99.999% purity was bubbled through to remove CO_2 and to stir the solution. A Crison microBU 2030 automatic burette furnished with a 2.5 ml syringe for dispensing the titrant was used. The burette was controlled *via* a computer which performed the readings of the potential difference of a Crison micropH 2002 *pH*-meter connected to a glass electrode. The following electrodes were used: (a) Electrode without liquid junction, a Radiometer G202B single glass electrode, which was used with an Ag/AgCl electrode prepared in the laboratory following the thermal electrolytic method described in Ref. [42]. $AgNO_3$ (Merck, p.a.) was used to obtain the silver oxide by precipitation. Constant boiling point HCl was obtained from HCl from Merck (suprapur) as it is described in Ref. [44]. (b) Electrode with liquid junction, a Radiometer GK2401C combination glass electrode with Ag/AgCl as reference electrode. The liquid junction was a plug of porous ceramics. The solution of the external reference electrode was saturated KCl.

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