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Analysis of systematic errors in calibrating glass electrodes with H^+ as a concentration probe

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Summary. Two different experimental methods for the calibration of glass electrodes for H^+ concentration are analysed: strong acid – strong base titration and addition of the strong base or acid to the solvent. Possible systematic errors in acid or base concentrations used for calibration affect in a different way the linear relationship between the cell potential and the logarithm of the hydrogen ion concentration in each case. We have examined how such errors influence the slope of the calibration curve by using a programme that simulates the calibration procedure and we have compared this analysis with some experimental results previously obtained.

Introduction

The experimental determination of the stoichiometric acid-base equilibrium constants requires the proton concentration $[H^+]$ to be known; on the other hand, the potential measured potentiometrically by using glass electrodes is really a function of the activity a_{H^+} of H^+ ions in solution according to the well-known relation:

$$E_{cell} = E_k + s \log a_{H^+} , \tag{1}$$

where

$$E_k = E_g^0 + E_r + E_{lj} , \tag{2}$$

being E_g, E_r and E_{lj} the standard (including the asymmetry potential), reference and liquid junction potentials, respectively. Although, for a long time, it has been demonstrated that the liquid junction potential depends on the acidity of the medium and some mathematical expressions have been used in the literature to take this effect into account [1], this potential however can be assumed to be constant over certain narrow acidity ranges [2].

In addition, when the approximation of the constant ionic medium is used by adding a background electrolyte, activity coefficients of the species present can also be considered to remain constant; thus, under these circumstances, a linear relationship between measured potential of the cell and the logarithm of the H^+ concentration can be established:

$$E_{cell} = E^I_{const.} + s \log [H^+] , \tag{3}$$

where

$$E^I_{const.} = E_k + s \log \gamma_{H^+} . \tag{4}$$

The most usual calibration method in this context (E vs. log $[H^+]$) involves performing a strong acid – strong base titration in order to obtain $E^I_{const.}$ and s for a given ionic medium. An alternative procedure entails determining the proton concentration by adding an acid or base to the solvent used, the titration being performed in an acid or basic medium. The equations for obtaining the proton concentration differ in each case, which will be the basis for discussing the influence of some systematic errors that may arise depending on the particular calibration procedure used.

Experimental

All reagents used were Merck P. A. chemicals. The water used to prepare the solutions was purified by passage through a Millipore-MilliQ system and subsequently boiled to remove CO_2. Potential measurements were made by means of a Radiometer Copenhagen PHM 84 (36R37NO71) pH-meter. The titration cell was one of the typical models used in potentiometry, and through the solution held in it was passed a stream of high-purity nitrogen (99.999%). The temperature within the cell was kept at 298 ± 0.1 K throughout the experiments. Both real and simulated experiments were carried out over the ranges $2.3 \leq -\log [H^+] \leq 2.9$ and $2.7 \leq -\log [OH^-] \leq 3.2$, as recommended by several authors [3].

Results and discussion

In performing the potentiometric calibration by plotting the measured potential against the proton concentration in different background electrolytes we observed some interesting facts, i.e.: in some calibrations based on a strong acid – strong base titration, the slope of the plot E vs. $-\log [H^+]$ was larger or smaller than the Nernstian slope if the titration was affected in an acid or basic medium, respectively. On the other hand, if the calibration was performed by adding

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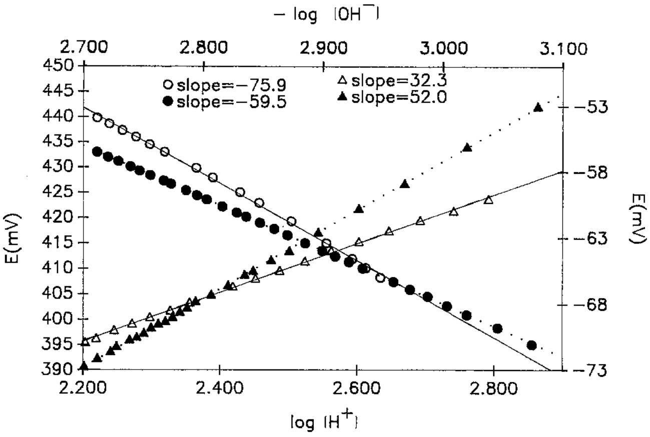

Fig. 1. ○,△ Calibration of the glass electrode by strong acid–strong base titration. Ionic strength 1.00 mol/l NaCl; titration of 0.015 mol/l HCl with 0.101 mol/l of NaOH. ●,▲ Calibration of the glass electrode by addition of strong acid (base) to the solvent. Ionic strength 1.00 mol/l NaCl; addition of 0.101 mol/l ClH or of 0.099 mol/l NaOH

the strong acid or base to the background electrolyte and using the same concentrations of acid or basic titrant, the slope of the plot was very close to the theoretical prediction of the Nernst equation and the plot of E vs. $-\log [H^+]$/$-\log [OH^-]$ was linear (Fig. 1), which reveals the glass electrode used to exhibit a Nernstian behaviour. We ascribed the above findings to the influence of certain systematic errors made in the acid or base concentration on the equations governing the acid–base titration in one case and the addition process in the other.

Procedure 1. Strong acid–strong base titration

In this case, the proton concentration is given by:

$$[H^+] = \frac{c_a V_0 - c_b v}{V_0 + v} \tag{5}$$

before the equivalent point, and the hydroxyl concentration by:

$$[OH^-] = \frac{c_b v - c_a V_0}{V_0 + v} \tag{6}$$

after it, where c_a is the concentration and V_0 the volume of strong acid before the titration, and c_b and v denote the concentration of base added and the added base volume. Equation (5) can be rewritten as:

$$[H^+] = \frac{c_a - c_b x}{1 + x}, \tag{7}$$

where $x = v/V_0$.

Substitution of Eq. (7) into Eq. (3) yields:

$$E_{cell} = E^{I}_{const} + s \log \frac{c_a - c_b x}{1 + x}. \tag{8}$$

In the basic region, the concentration of hydroxyl ions can be obtained from Eq. (6) or, alternatively, from

$$[OH^-] = \frac{c_b x - c_a}{1 + x}; \tag{9}$$

so that:

$$E_{cell} = E^{II}_{const} + s \log \frac{c_b x - c_a}{1 + x}. \tag{10}$$

Procedure 2. Concentration of the solution: addition of a strong acid or base to the solvent

In this case, volumes of a strong acid or base are successively added to an initial background electrolyte volume V_0. Thus, the concentration of acid (or base) will be given by:

$$[H^+] = \frac{C_i v}{V_0 + v} = \frac{C_i x}{1 + x}. \tag{11}$$

It is worth noting that when $x \ll 1$ (or $v \ll V_0$), then $[H^+]$ or $[OH^-] = C_i x$, where C_i is the concentration of acid or base and v the added volume. Equation (3) thus becomes:

$$E_{cell} = E^{IV}_{const} + s \log \frac{x}{1 + x}, \tag{12}$$

where:

$$E^{IV}_{const} = E^{III}_{const} + s \log C_i. \tag{13}$$

In mathematical terms, the two calibration procedures differ in that the logarithmic term in Eqs. (8) and (10) is a function not only of x and Eq. (12) is a function of x only; therefore any systematic errors made in the analytical concentrations c_a and c_b should affect the slope and intercept of the fittings to a different extent.

In fact, as can be clearly seen from Eqs. (12) and (13), a systematic error made in C_i should have no effect on the slope of the fitting (s); therefore, if the electrode exhibits a Nernstian response, it will do so irrespective of any errors made in C_i – this is consistent with the experimental observations (Fig. 1). In the basic region, the deviations with respect to 59 mV can be ascribed to the influence of the Na^+ ion in terms of the so-called alkaline error [4, 5].

Equations (8)–(10), however, cannot be applied to the above reasoning; in fact, because of the very nature of the equations, errors in the slope and the intercept of the fitting should arise from any errors made in c_a and c_b. Let us denote such systematic errors by:

$$J_i = \frac{C_{i,w}}{C_{i,f}} \quad (i = a,b), \tag{14}$$

where $C_{i,w}$ and $C_{i,f}$ are the concentrations of the acid (or basic) titrant subjected to an error and that free from it, respectively. Equation (8) can now be rewritten, for instance, as:

$$E_{cell} = E_{const} + s \log \frac{j_a c_{a,w} - j_b c_{b,f} x}{1 + x}. \tag{15}$$

Simulated calibration

We simulated the behaviour of Eq. (15) for different combinations of the parameters j_a and j_b according to the following procedure:

1. E_{cell} values were obtained from Eqs. (8) and (10) with $j_a = j_b = 1$, $E = 100$ mV and $s = 59$ mV. The acid and base concentration, and the solution volume ($V_0 = 40$ ml) were consistent with the real values used in the experimental calibration.

Table 1. Simulation of a calibration for the titration of a strong acid (0.01 mol/l) with a strong base (0.1 mol/l) in the acid region (* denotes the same j_a, j_b values in Tables 1 and 2), r denotes the correlation coefficient

j_a	j_b	E_{const}	s	r
1.00	1.00	100.003 ± 0.2	−58.999 ± 0.1	1.0000
*1.00	0.99	95.225 ± 2.5	−61.133 ± 0.9	0.9999
*1.05	1.03	92.214 ± 3.3	−63.082 ± 1.3	0.9999
*1.03	1.01	91.514 ± 3.3	−63.160 ± 1.3	0.9999
*1.01	0.99	90.787 ± 3.4	−63.245 ± 1.3	0.9999
*0.99	0.97	90.047 ± 3.4	−63.331 ± 1.3	0.9999
*0.97	0.95	89.282 ± 3.5	−63.421 ± 1.4	0.9999
*1.03	1.00	86.831 ± 4.0	−65.279 ± 1.6	0.9999
*1.00	0.97	85.576 ± 4.1	−65.467 ± 1.6	0.9999
*1.05	1.01	83.042 ± 4.5	−67.255 ± 1.8	0.9999
*1.03	0.99	82.126 ± 4.5	−67.416 ± 1.8	0.9999
*1.01	0.97	81.176 ± 4.6	−67.586 ± 1.8	0.9999
*0.99	0.95	80.187 ± 4.7	−67.768 ± 1.8	0.9999
*1.05	1.00	78.411 ± 4.9	−69.373 ± 1.9	0.9999
*1.00	0.95	75.760 ± 5.1	−69.908 ± 2.0	0.9999
*1.05	0.99	73.724 ± 5.3	−71.523 ± 2.2	0.9999
*1.03	0.97	72.566 ± 5.4	−71.778 ± 2.2	0.9999
*1.01	0.95	71.383 ± 5.5	−72.039 ± 2.2	0.9999
1.05	0.97	64.194 ± 6.0	−75.913 ± 2.4	0.9999
1.03	0.95	62.809 ± 6.0	−76.258 ± 2.4	0.9999
1.01	1.00	58.291 ± 6.3	−79.389 ± 2.6	0.9999
1.05	0.95	54.449 ± 6.5	−80.428 ± 2.7	0.9999
1.00	1.01	104.752 ± 2.6	−56.887 ± 1.0	0.9999
0.99	1.00	104.552 ± 2.6	−56.865 ± 1.0	0.9999
1.03	1.05	109.915 ± 3.6	−54.912 ± 1.4	0.9999
1.01	1.03	109.628 ± 3.7	−54.832 ± 1.4	0.9999
0.99	1.01	109.331 ± 3.7	−54.752 ± 1.4	0.9999
0.97	0.99	109.050 ± 3.8	−54.662 ± 1.5	0.9999
0.95	0.97	108.761 ± 3.8	−54.572 ± 1.5	0.9999
1.00	1.03	114.205 ± 4.6	−52.709 ± 1.8	0.9999
0.97	1.00	113.947 ± 4.7	−52.516 ± 1.8	0.9999
1.01	1.05	118.954 ± 5.4	−50.721 ± 2.1	0.9999
0.99	1.03	118.893 ± 5.5	−50.555 ± 2.1	0.9999
0.97	1.01	118.839 ± 5.6	−50.383 ± 2.1	0.9999
0.95	0.99	118.798 ± 5.7	−50.203 ± 2.2	0.9999
1.00	1.05	123.643 ± 6.3	−48.578 ± 2.4	0.9999
0.95	1.00	123.824 ± 6.6	−48.033 ± 2.5	0.9999
0.99	1.05	128.480 ± 7.1	−46.390 ± 2.7	0.9999
0.97	1.03	128.669 ± 7.3	−46.132 ± 2.7	0.9999
0.95	1.01	128.876 ± 7.4	−45.864 ± 2.8	0.9999
0.97	1.05	138.660 ± 8.9	−41.864 ± 3.3	0.9999
0.95	1.03	139.140 ± 9.1	−41.501 ± 3.4	0.9999
0.95	1.05	149.799 ± 11.0	−37.038 ± 4.0	0.9999

Table 2. Simulation of the calibration for the titration of a strong acid (0.01 mol/l) with a strong base (0.1 mol/l) in the basic region. (* as described in Table 1), r denotes the correlation coefficient

j_a	j_b	E_{const}	s	r
1.00	1.00	99.994 ± 0.3	58.998 ± 0.1	1.0000
1.00	1.01	111.008 ± 5.6	63.569 ± 1.2	0.9999
0.99	1.00	111.394 ± 3.6	63.615 ± 1.2	0.9999
1.03	1.05	120.048 ± 4.7	67.753 ± 1.7	0.9999
1.01	1.03	121.029 ± 4.8	67.925 ± 1.7	0.9999
0.99	1.01	122.026 ± 4.8	68.098 ± 1.7	0.9999
0.97	0.99	123.062 ± 4.9	68.281 ± 1.7	0.9999
0.95	0.97	124.119 ± 4.9	68.466 ± 1.7	0.9999
0.97	1.00	133.460 ± 5.7	72.725 ± 2.0	0.9999
1.01	1.05	140.547 ± 6.1	76.380 ± 2.2	0.9999
0.99	1.03	141.974 ± 6.2	76.714 ± 2.2	0.9999
0.97	1.01	143.435 ± 6.3	77.056 ± 2.2	0.9999
0.95	0.99	144.962 ± 6.3	77.418 ± 2.3	0.9999
1.00	1.05	150.566 ± 6.6	80.664 ± 2.4	0.9999
0.95	1.00	154.783 ± 6.8	81.733 ± 2.4	0.9999
0.99	1.05	160.442 ± 7.0	84.931 ± 2.6	0.9999
0.97	1.03	162.314 ± 7.0	85.432 ± 2.6	0.9999
0.95	1.01	164.231 ± 7.1	85.946 ± 2.6	0.9999
0.97	1.05	179.883 ± 7.5	93.444 ± 2.8	0.9999
0.95	1.03	182.146 ± 7.6	94.098 ± 2.8	0.9999
0.95	1.05	198.899 ± 7.9	101.919 ± 3.0	0.9999
1.01	1.00	88.296 ± 4.0	54.327 ± 1.4	0.9999
*1.00	0.99	88.411 ± 4.0	54.279 ± 1.4	0.9999
*1.05	1.03	76.254 ± 6.0	49.845 ± 2.0	0.9999
*1.03	1.01	76.209 ± 6.0	49.662 ± 2.0	0.9999
*1.01	0.99	76.146 ± 6.1	49.469 ± 2.0	0.9999
*0.99	0.97	76.072 ± 6.2	49.270 ± 2.1	0.9999
*0.97	0.95	75.971 ± 6.3	49.059 ± 2.1	0.9999
*1.03	1.00	63.537 ± 8.0	44.686 ± 2.6	0.9999
*1.00	0.97	62.916 ± 8.2	44.225 ± 2.7	0.9999
*1.05	1.01	50.535 ± 10.0	39.830 ± 3.3	0.9999
*1.02	0.99	49.766 ± 10.0	39.414 ± 3.3	0.9999
*1.01	0.97	48.947 ± 10.0	38.980 ± 3.4	0.9999
*0.99	0.95	48.069 ± 11.0	38.525 ± 3.4	0.9999
*1.05	1.00	35.606 ± 12.0	34.253 ± 4.0	0.9999
*1.00	0.95	32.207 ± 13.0	32.756 ± 4.2	0.9999
*1.05	0.99	17.850 ± 16.0	27.864 ± 5.0	0.9999
*1.03	0.97	15.679 ± 16.0	27.024 ± 5.1	0.9999
*1.01	0.95	13.288 ± 17.0	26.116 ± 5.3	0.9999

2. From these initial data, the programme calculated the corresponding potential (E) and log $[H^+]$ at each v (added volume) value.

3. By using a random number generating programme [6] with a normal distribution, each E value was converted to the average of 50 values subject to a given standard deviation. Accordingly, for each E(v) value obtained from the initial data a new E′(v) value was calculated given by:

$$E'(v) = \frac{[(E(v) + d_1) + (E(v) + d_2) + \ldots + (E(v) + d_{50})]}{N} \tag{16}$$

where d_i (≤ 0.005) denotes the different standard deviations.

4. After introducing variations in the acid and base concentrations via parameters j_a and j_b the programme calculated log $[H^+]$.

5. A least-square fitting in the form $E'(v) = a(-\log[H^+]) + b$ was then performed.

6. Finally, the E_{const} and s values for different combinations of j_a and j_b were calculated.

Tables 1 and 2 list the results obtained in a typical simulation. j_i values are referred to variations within ±5 %. As the difference between j_a and j_b increases, the fitting parameters deviate markedly from the values predicted by the initial calculations. Also, for a given pair of j_a and j_b values, deviations are more marked in the basic than in the acid region, which is consistent with the experimental observations. In addition, given combinations of systematic errors in the concentration of acid and base (denoted by asterisks in Tables 1 and 2) result in increased slopes for the acid medium and decreased slopes for the basic medium, which is also consistent with the experimental observation.

Conclusions

From the above discussion it follows that the occurrence of systematic errors in the concentration of an acid or basic titrant results in different effects on the electrode response, depending on the characteristic form of the equation on which the calibration procedure relies. A calibration by addition of a strong acid or base to a background electrolyte allows to determine whether – and to what extent – the electrode exhibits a Nernstian behaviour; however, it is insensitive to systematic errors, which clearly arise in strong acid–strong base calibrations and increase or decrease the slopes of the fittings with respect to a theoretical value in the acid and/or basic titration region. Although, as stated elsewhere [7], the magnitude of systematic errors in complex equations (e.g. those describing complex equilibria) is difficult to determine as errors propagate in the equations in rather an intricate manner, the indices j_a and j_b used here can be determined by optimization procedures [8]. We used one such procedure to analyze the influence of systematic errors on the pK-values of simple equilibria [9].

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