The influence of high ionic strength on the potentiometric determination of pH 4.0 (25 °c, $I = 1.0$ mol L^{-1}) in acidified brine of preserved hearts of palm

A influência da alta força iônica na determinação potenciométrica de pH 4,0 (25 °c, $I = 1,0$ mol L^{-1}) em salmoura acidificada de corações de palma conservados

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ABSTRACT

The aim of this study was to evaluate the influence of ionic strength (I) on the potentiometric pH measurement of solutions with high I such as the Acidified Brine of Preserved Hearts of Palm (ABPHP) as it is accurately measured only in dilute solutions where $I \leq 0.1$ mol L^{-1} as defined by Debye-Hückel's theory. Standard calibrators were developed to evaluate a potassium biphthalate buffer solution (BS4: pH 4.0 at 25 °C) with the variation of I of the medium. In practical application, the objective is the optimization of the potentiometric pH measurements of solutions having high I, for example, ABPHP with an I of 0.98 mol L^{-1} [1]. The choice of this procedure is justified because ABPHP has a naturally high I that is not consistent with Debye-Hückel's theory. This can make pH measurements unreliable. From a public health point of view, the botulism often implicated these preserved vegetables, and the potentiometric pH measurement is the only legal parameter for quality control employed to improve sanitary control actions. The quantitative variables (position and dispersion) were calculated as mean, maximum and minimum values, standard deviation and coefficient of variation. Moreover, the Grubbs' test was used to identify possible outliers and their homogeneity, thereby demonstrating the linear tendency of the results. Student's t-test and ANOVA with a 95% confidence index were used to verify the variability of the results. The results are promising, since by altering the I of the medium ($I > 0.1$ mol L^{-1}), there was a change in the pH of the solution. This study is important to ensure a true quality control in the production of preserved hearts of palm.

Keywords: public health, hydrogenation potential, hearts of palm.

RESUMO

O objetivo deste estudo foi avaliar a influência da força iônica (I) na medição potenciométrica do pH de soluções com I elevado, como a salmoura acidificada de palmito conservado (ABPHP), pois é medida com precisão apenas em soluções diluídas onde I 0,1 mol L-1 como definido pela teoria de Debye-Hückel. Os calibradores padrão foram desenvolvidos para avaliar uma solução tampão de biftalato de potássio (BS4: pH 4,0 a 25 °C) com a variação de I do meio. Na aplicação prática, o objetivo é a otimização das medições potenciométricas de pH de soluções com I elevado, por exemplo, ABPHP com I de 0,98 mol L-1 (1). A escolha deste procedimento é justificada porque a ABPHP tem um I naturalmente alto que não é consistente com a teoria de Debye-Hückel. Isto

pode tornar as medições de pH pouco confiáveis. Do ponto de vista da saúde pública, o botulismo muitas vezes implicou nestes vegetais preservados, e a medição potenciométrica do pH é o único parâmetro legal para o controle de qualidade empregado para melhorar as ações de controle sanitário. As variáveis quantitativas (posição e dispersão) foram calculadas como média, valores máximos e mínimos, desvio padrão e coeficiente de variação. Além disso, o teste de Grubbs foi utilizado para identificar possíveis aberturas e sua homogeneidade, demonstrando assim a tendência linear dos resultados. O teste t de Student e ANOVA com um índice de confiança de 95% foram usados para verificar a variabilidade dos resultados. Os resultados são promissores, pois ao alterar o I do meio
(I > 0,1 mol L-1), houve uma mudança no pH da solução. Este estudo é importante para garantir um verdadeiro controle de qualidade na produção de corações de palma conservados.

Palavras-chave: saúde pública, potencial de hidrogenação, corações de palma.

1 INTRODUCTION

Potentiometric pH measurement using a glass electrode is carried out in large scale in the routines of chemical, biochemical and industrial laboratories, clinical analysis, food analysis as well as in universities, in line measurement companies, remote measurements in large lakes and oceans, and in research centers. Thus, this is probably the most widely used measurement among the instrumental techniques used in the field of chemistry[2]. As this method is classified as a secondary method of measurement, it depends on standards traceable to the primary method[3]. Hence, the use of certified reference materials (CRM) as a way of guaranteeing the traceability of measurements is important[4].

This procedure does not guarantee that measurement uncertainty is adequate for a given objective, without which the results obtained can adversely affect health. For example, one of the most important factors in the processing of hearts of palm is the acidification of the brine to inhibit the bacteria that causes botulism. For this reason, the potentiometric pH measurement is of fundamental importance because it is a quality control parameter[5, 6].

This study is to investigate the influence of ionic strength (I) on potentiometric pH measurements. This measure is used in sanitary control actions directed toward preserved vegetables, particularly preserved hearts of palm due to their implication in botulism[7, 8 (a, b)]. In this case, acidified brine of preserved hearts of palm (ABPHP)[1] has an I of 0.98 mol L^{-1} and potentiometric pH measurements are only accurate in dilute solutions with $I \leq 0.1$ mol L^{-1} according to the estimate given by Debye-Hückel's theory[9].

This theory takes into account the effects of electrostatic interactions between ions in solution. The intensity of the electric field due to the presence of ions in solution is quantified by means of the parameter *I* as introduced by Lewis and Randall. It is important to remember that *I* affect the concentration of an ionic species in solution. This property changes the reactive capacity of the ions in the solution due to the electrostatic interactions (attraction and repulsion) between them. These interactions become more pronounced as the concentration increases.

Standard calibrators were developed to evaluate the potassium biphthalate buffer solution (BS4: pH 4.0 at 25 °C) with the variation of *I* of the medium. In practical application, improvements in the potentiometric pH measurements of solutions with a high *I* are desired.

1.1 DEFINITION OF PH

The pH is defined in terms of the activity of the H$^+$ (a_{H+}). The coefficient of activity of a single ion γ_{H^+} and all others involved in the equilibrium with H$^+$ in aqueous solution are estimated using the Debye-Hückel's electrostatic theory which has its validity limited to dilute solutions where *I* is ≤ 0.1 mol L^{-1}, as described in Equation 1.

$$pH = -\log a_{H^+} = -\log(\gamma_{H^+} m_{H^+}) \quad (1)$$

Thus, solutions with higher *I*, as in the case of ABPHP, require special studies due to their non-ideal behavior caused by the interactions between the ions. The ideal pH for food safety can be calculated by the Henderson-Hasselbalch equation according to Equation 2[10, 11].

$$pH = pKa + \log\left(\frac{[X^-]}{[HX]}\right) \quad (2)$$

In order to proceed to investigate sources of uncertainty we use the model to determine the pH described in Equation 3.

$$pH_x = \frac{(E_x - E_1)}{S(1+\alpha\Delta T)} + pH_1 \quad (3)$$

Where:

pH $_x$ = pH of an unknown solution;

E_x = cell potential for the unknown solution;

pH_1 = pH of the standard solution;

E_1 = cell potential for the standard solution;

S = Nernst equation (3.303 RT/nF where: n = 1, F = 96485. 3383 C mol^{-1}, R = 8.314472 J K^{-1} mol^{-1});

α = average temperature coefficient of the glass electrodes = (3.21 x 10^{-3} ± 0.53 x 10^{-3} K^{-1});

ΔT = temperature change during measurement.

1.2 THE SOURCES OF UNCERTAINTIES OF THE PREDICTED PH

The uncertainty of CRM pH 4.00 is expressed in the supplier's catalog. Initially, the standard uncertainty is calculated considering a normal distribution (Equation 4):

$$u(pH_{MRC}) = \frac{0.01}{1.96} = 0.0051 \qquad (4)$$

By combining the standard uncertainties from the certificate and from the effect of temperature variations, the uncertainty of the pH of the buffer solution (pH 4.00) is obtained according to Equation 5.

$$u_{(pH4,00)} = \sqrt{u^2_{(pHMRC)} + u^2_{(pH\Delta T)}} \qquad (5)$$

The resolution of the potentiometer used was pH 0.01 and the uncertainty from the resolution was considered to be half of its smallest division and the distribution as triangular. The expanded uncertainty of the calibration certificate is 0.02 pH and the rectangular distribution considered (Equation 6)[13, 14]:

$$u_{pHmeter} = \sqrt{\left(\frac{0.01}{2\sqrt{6}}\right)^2 + \left(\frac{0.020}{2\sqrt{3}}\right)^2} = 0.006124 \qquad (6)$$

The concept of pH, strictly speaking, only applies to dilute aqueous solutions. This shows the importance of the ionic product of water (Kw) in the establishment of pH. This also illustrates that the pH scale values are not arbitrary but originate from the experimental measurement of Kw: as Kw varies with temperature, the pH range will also vary.

These considerations corroborate the need to validate the method and estimate the uncertainty of the measurement using a standard with *I* being similar to that of ABPHP, since the legal standard establishes a maximum pH of 4.5 for preserved hearts of palm in order to guarantee the safety of the product in respect to botulism. It should be noted that common routine calibrators as well as commercial CRMs for pH measurement do not state the *I* and the ions of ABPHP in their compositions.

In the conventional manner, recommended by the National Institute of Standards and Technology (NIST) and DIN, the calibration of the pH electrode with standards (solutions with known pH) allows measurements by comparison and with the estimated uncertainty of the pH of unknown solutions.

Thus, it has become essential to verify the amount and how measurements using standard calibrators with an *I* similar to ABPHP differ from those routinely employed and commercially available.

1.3 STANDARD BUFFER SOLUTIONS

The primary method to measure pH uses the HARNED cell (without liquid junction) and standards that are not referenced from other standards because they are high quality primary solutions with low uncertainty. Secondary methods, however, use liquid junction cells whose potentials are not fully known. The secondary standards present greater uncertainties and the values assigned to them are by comparison to the primary standards[15].

The pH of the primary and secondary standard solutions depends on the Debye-Hückel's equation to obtain the activity coefficient to calculate the pH. This equation can be experimentally tested for solutions with up to 1 mol L^{-1} of I[16, 17].

Limitation of potentiometric pH measurement

The potentiometric pH measurement with combined glass electrode has associated uncertainty as it depends on a secondary standard and the contribution of the potential difference between the liquid in the electrode and the standard (or sample). This potential difference is not completely known. It depends on the temperature, the concentration of

the salt bridge and the solution in the electrode. It can be considered constant since it is not a thermodynamically measurable variable.

2 MATERIAL AND METHODS

2.1 PREPARATION OF SOLUTIONS

2.1.1 Citric Acid 0.036 mol L^{-1}

Citric acid ($C_6H_8O_7$) was oven dried at 110 °C, weighed 1.7309 g and dissolved in 250 mL deionized water.

2.1.2 Buffer solution (BS4f)

2.1.2.1 Buffer Solution (BS4f)

For final solution at pH 4, 10.2 mL of Solution 1 and 12.3 mL of Solution 2 were mixed, that:

2.1.3 Solution 1

Disodium phosphate salt (Na_2HPO_4) (Vetec, code 317, lot 1005032, purity 99.0%) oven dried at 110 °C for 1 hour; weighed 4.459 g (Scales Mettler Toledo, model PR1203, resolution 0.001 g) was dissolved in 250 mL deionized water [initial electrolytic conductivity less than 0.1 µS cm^{-1} (SM4500H$^+$)] and homogenized.

2.1.4 Solution 2

Citric acid ($C_6H_8O_7$) (Dynamic, code 1260, lot 68944, purity 99 to 102%) oven dried at 110 °C for 1 hour; weighed 5.253 g (Scales Mettler Toledo, model PR1203, resolution 0.001 g) was dissolved in 250 mL deionized water [initial electrolytic conductivity less than 0.1 µS cm^{-1} (SM4500H$^+$)] and homogenized.

2.1.5 Buffer solution 0.05 mol L^{-1} (BS4)

Potassium hydrogen phthalate salt ($KHC_8H_4O_4$) (Vetec, code 354, lot 0800351, purity 99.9 to 100.05%) oven dried at 110 °C for 1 hour; weighed 25.304 g (Scales Mettler Toledo, model PR1203, resolution 0.001 g) was dissolved in 2.5 L deionized water [initial electrolytic conductivity less than 0.1 µS cm^{-1} (SM4500H$^+$)] and homogenized.

2.1.6 Sodium chloride 0.5 mol L⁻¹ and 1.0 mol L⁻¹

Sodium chloride (NaCl) dried in the oven at 110 °C, weighed the quantities to maintain the concentration of 0.5 mol L^{-1} and 1.0 mol L^{-1} in 10 mL of BS4 solutions.

2.1.7 Acidified Brine of Preserved Hearts of Palm (ABPHP)

Sodium chloride (NaCl) and citric acid ($C_6H_8O_7$) were oven dried at 110 °C; weighed 112.500 g and 17.500 g, respectively and dissolved in 2.5 L of deionized water. The final concentrations of the NaCl and citric acid in the ABPHP are 0.77 mol L^{-1} and 0.036 mol L^{-1}, respectively.

2.1.8 Calibration check and pH measurements

To adjust the pH measurement system (potentiometer: Analion model PM 608, with precision of ± 0.01 pH and ± 1 mV, input resistance of 10^{13} ohms, and Analion combined glass electrode, model V 620) commercial buffering solutions (pH 4 and 7) and CRM were used as well as solutions prepared in the laboratory with the following specifications:

-        Commercial Buffer Solution (Analion):

pH 4.01 at 25 °C, LOT: 7192
pH 7.00 at 25 °C, LOT: 7193

In the absence of commercial CRM with an *I* similar to that of the ABPHP, the CRM available used as specified below:
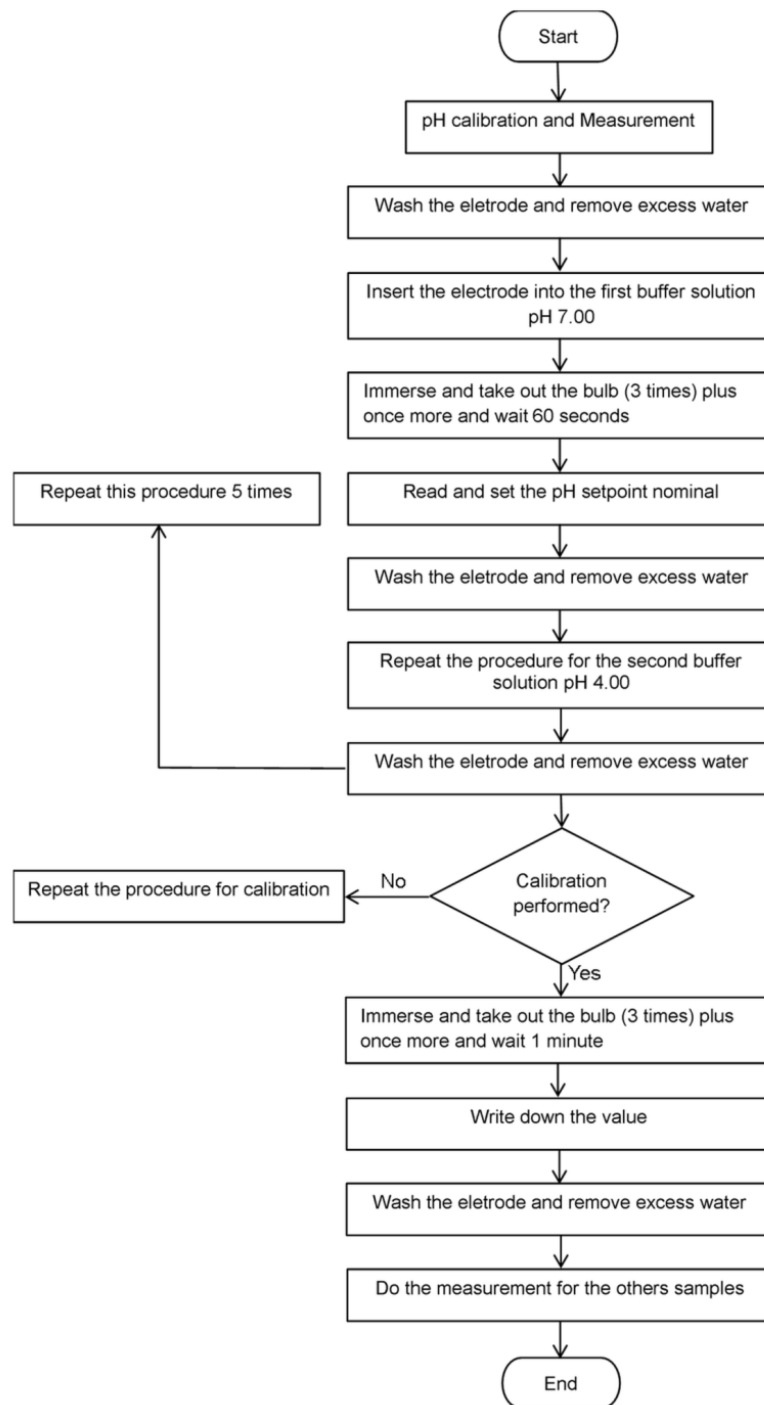
-        CRM (Quemis):

-
pH (4.00 ± 0.01) at 25 ± 0.2 °C, LOT: F09F058F
pH (7.00 ± 0.01) to (25 ± 0.2) °C, LOT: F09D009E

The procedure had the following steps[18], as the Figure 1:

Figure 1 - Schematic representation of the calibration and pH measurement procedure

Source: own elaboration

2.2 STUDIES RELATED TO THE IONIC STRENGHT

Since the I affects the ionization equilibrium and considering the constant I (fixed), γ (activity coefficient) does not change (Equation 9)

$$a_{H^+} = \gamma m_{} \qquad (9)$$

The study takes into account Equation 9 and the equilibria of auto ionization of water, ionization of citric acid (HCit), as well as of potassium biphthalate (KHP), Equations (chemical reactions)[19] 10, 11 and 12, respectively.

$$H_2O + H_2O \rightleftharpoons H_3O^+ \underset{Kw}{+} HO^- \tag{10}$$

$$\tag{11}$$

$$\tag{12}$$
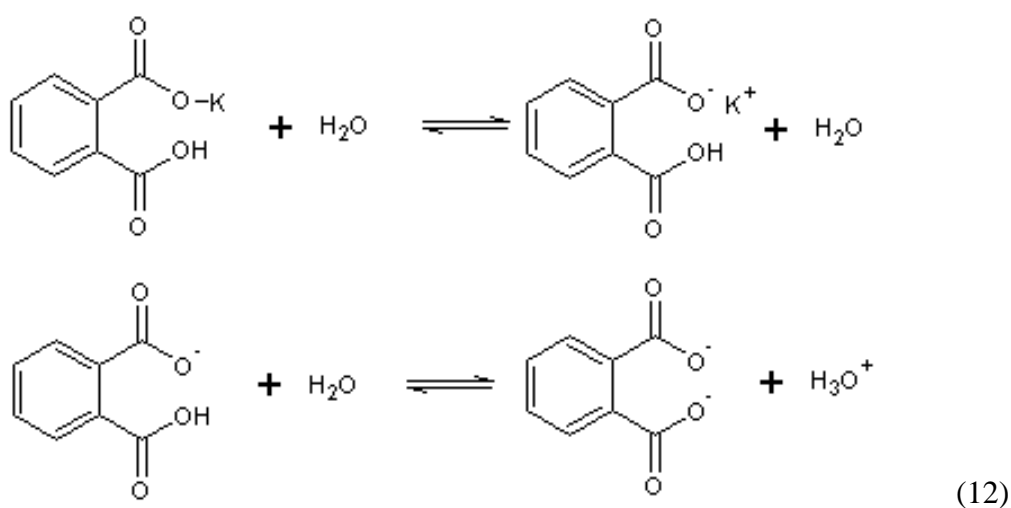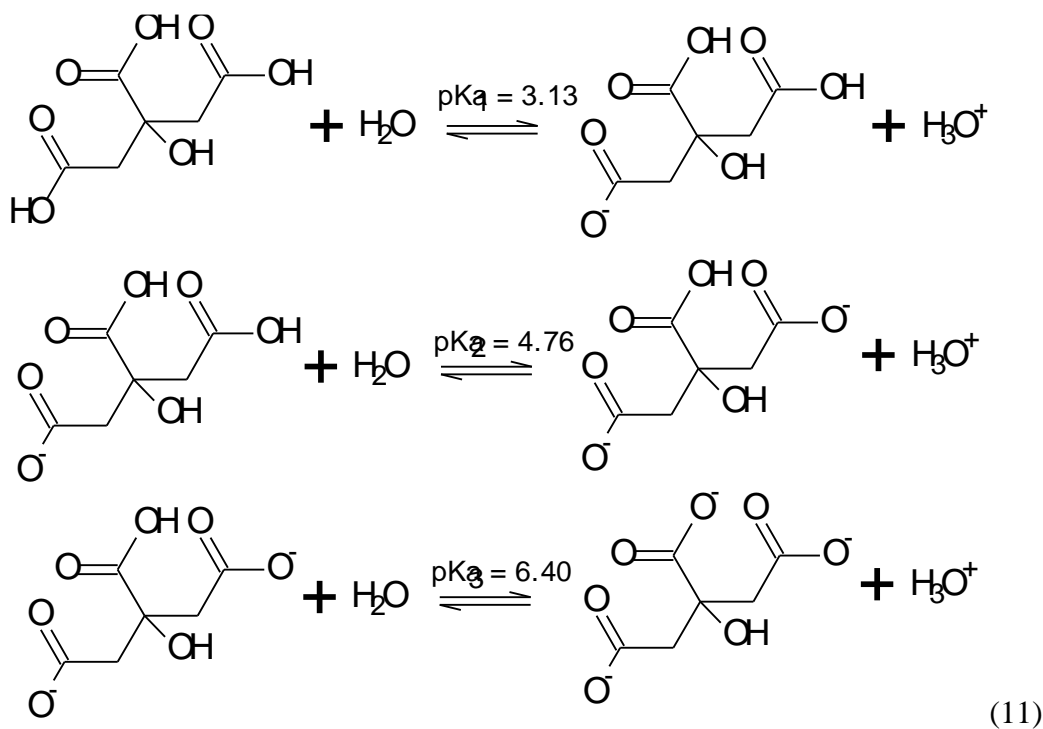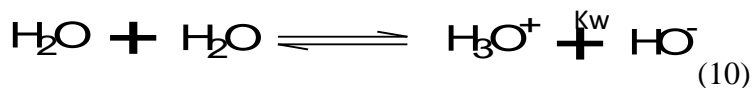
The equipment was adjusted with commercial buffer solutions. (pH 4.0 and 7.0) and CRM buffer solutions. All pH measurements were carried out five times. The pH of the following solutions were determined:

1) Citric Acid 0.036 mol L^{-1} solution, varying ionic strength ($0.095 \leq I \leq 2.005$) mol L^{-1},

2) Buffer solution with Disodium phosphate salt (Na_2HPO_4) and Citric acid ($C_6H_8O_7$) with nominal value pH = 4.00 (BS4f),

3) Buffer solution with nominal value of pH 4.00 (BS4),

4) Acidified Brine of Preserved Hearts of Palm (ABPHP).

3 RESULTS AND DISCUSSION

3.1 GRUBBS' TEST FOR OUTLIERS

For all measured data, was applied a criterion to exclude some outliers, such as Grubbs' Test, to set data to follow a normal distribution, so the Equation 16 was applied to each group of data and compared to *critical G value* 1.672[20] for n = 5 independent replicates at 95% of significance level.

$$G = \frac{\bar{y} - y_{min}}{s}$$

(13)

Where G is the Grubbs value to be tested against *critical G value*,

$\bar{y}$ = the mean value of pH measurements,

y_{min} = the minimum value obtained and,

s = the standard deviation.

3.2 IONIC STRENGTH STUDY

In order to evaluate the influence of I on the potentiometric pH of the citric acid at the same concentration (0.036 mol L^{-1}) used in the ABPHP, the different masses of NaCl were added to adjust the I ($0.095 \leq I \leq 2.005$) mol L^{-1}. The data obtained are illustrated in Figure 2.

Figure 2 - Distribution of the means of potentiometric pH measurements of citric acid 0.036 mol L^{-1} as a function of *I*
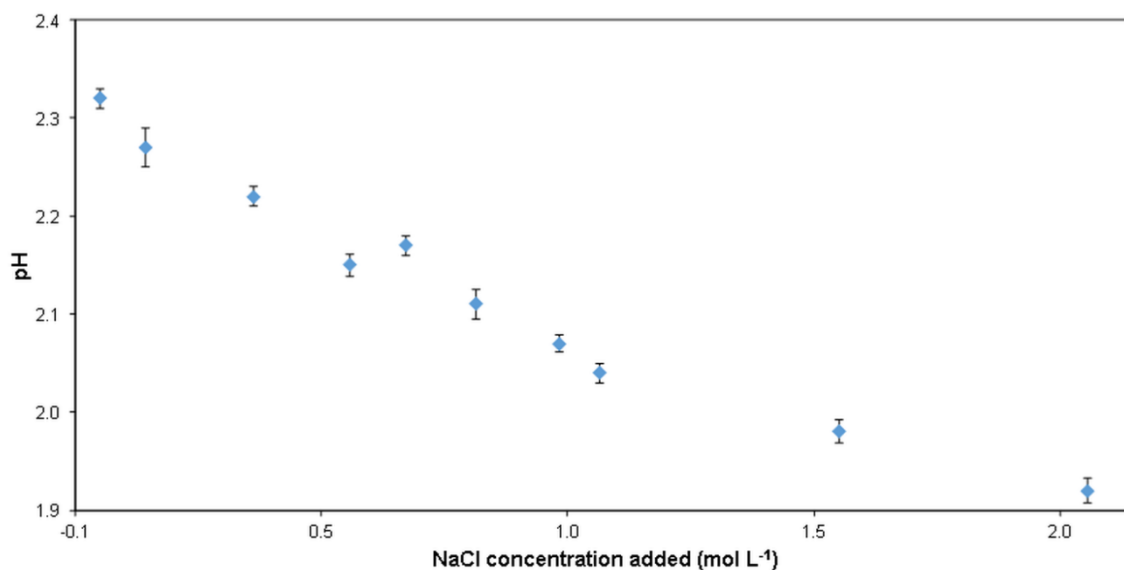
Source: own elaboration

The Figure 2 shows that the increase of *I* caused the pH to decrease. Accordingly, what can be evaluated is that at a higher *I* the H$^+$ activity is greater than in the initial citric acid 0.036 mol L^{-1}, i.e. the equilibria represented by Equations 10 and 11 have been altered.

The study revealed a direct relation between the activity coefficient (γ) and *I*, described for diluted solution in Debye-Hückel's theory, Equation 14[11].

$$\log(\gamma) = -A\, z^2\, I^{1/2} \qquad (14)$$

Where:

A = constant that depends on temperature,

z = charge number of ion.

This theory do not contemplate the solution in present work. For the study of the behavior of this solution, γ was monitored from the relation between initial concentration of H$^+$ and pH obtained from the addiction of NaCl. As consequence, the effective concentration of H$^+$ (activity) changed (Figure 3).

Figure 3 – The behavior of the activity as a function of the increase in activity coefficient (γ)
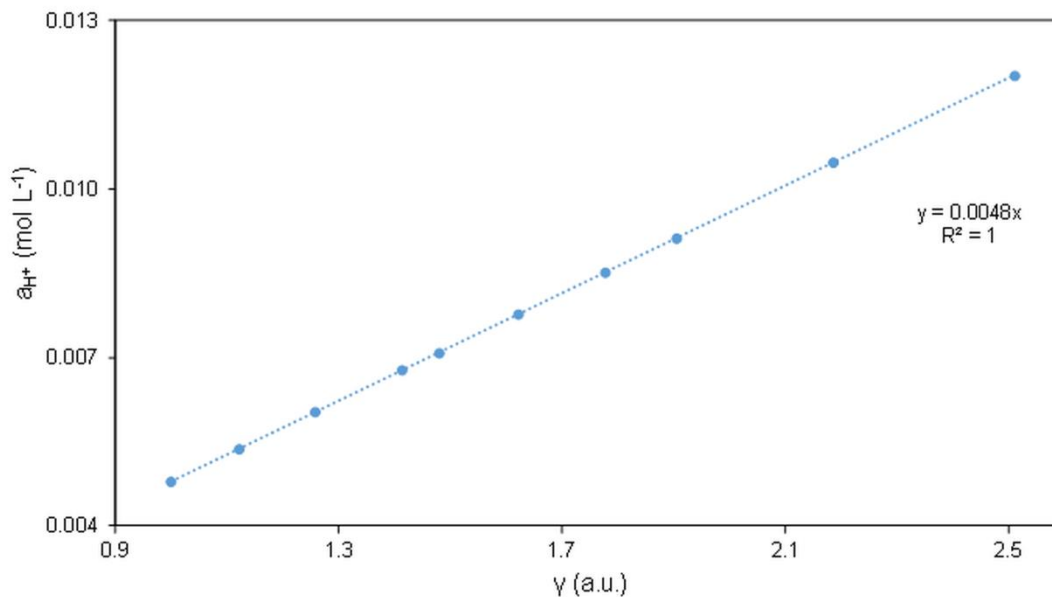
Source: own elaboration

Another buffer system (BS4f) was tested in order to establish the influence of *I* on the decreases of pH. The results obtained are shown in Figure 4.

Figure 4 - Distribution of the means of potentiometric pH measurements of BS4f as a function of NaCl concentration
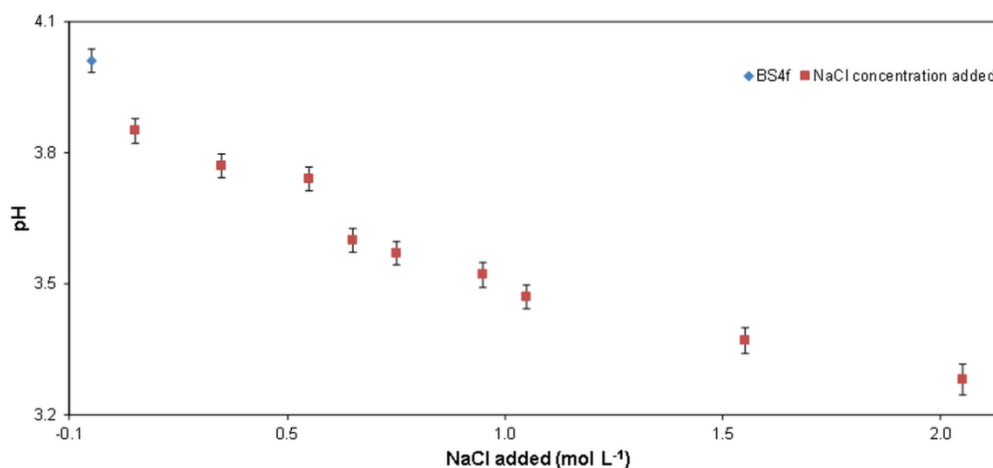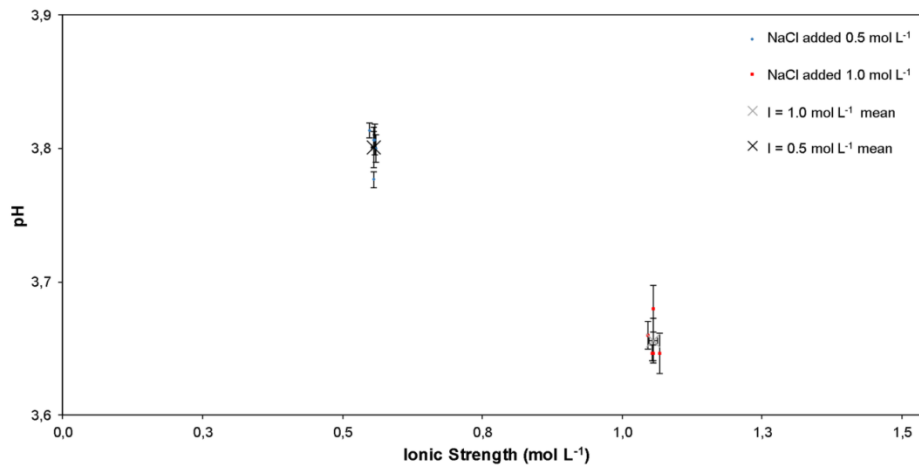

Source: own elaboration

BS4f presented the same behavior as the other systems, with the *I* varying at intervals very close to those previously studied although the profile of the graph shows greater dispersion. As additional information, there was no loss of buffering power in the range tested (Figure 4).

In order to evaluate the behavior of the BS4 system compared to the same *I* and the salt used to preserve vegetables, the sufficient NaCl added to obtain concentrations of 0.5 mol L^{-1} and 1.0 mol L^{-1} (Figure 5).

Figure 5 - Evaluation of the behavior of the means of potentiometric pH measurements of BS4 plus NaCl to obtain a concentration of 0.5 mol L^{-1} and 1.0 mol L^{-1}
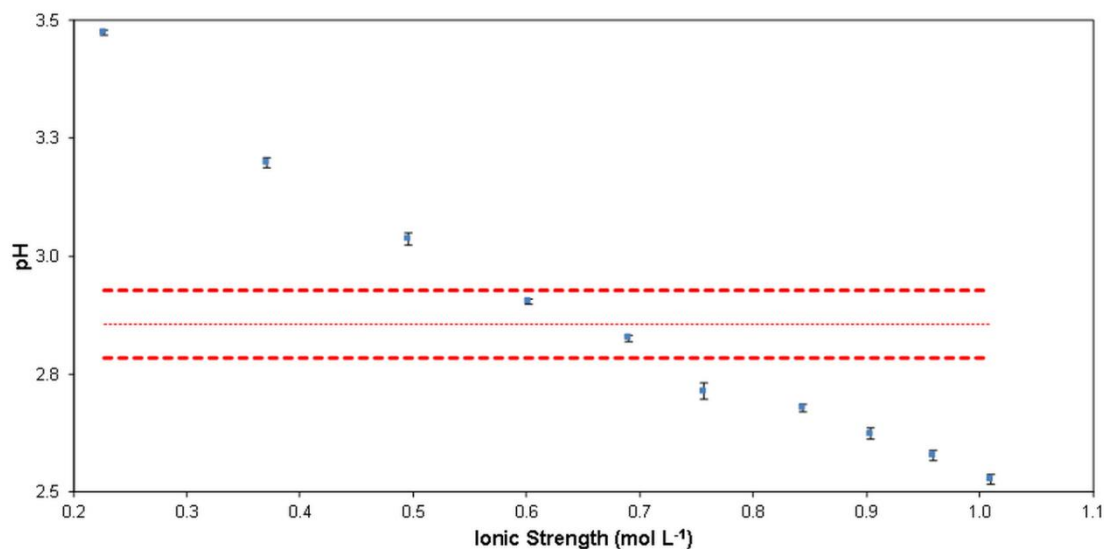

Source: own elaboration

Figure 5 shows a behavioral profile with similar pH variations between 0.5 mol L^{-1} and 1.0 mol L^{-1}, that is, the variations between the potentiometric pH measurements were 0.01 to 0.06.

The behavior of the tool representing the true situation of the potentiometric pH measurements, i.e. ABPHP with *I* of 0.98 mol L^{-1}, which is not in accordance with Debye-Hückel's theory, presented the profile shown by Figure 6.

Figure 6 - pH values as a function of the variation of *I* (addition of ABPHP to BS4) and upper and lower limits of ± 2.5% of the mean value

Source: own elaboration

In Figure 6, it can be considered that the volume increments (mL) of ABPHP in the BS4 system, by increasing the *I*, caused the buffer capacity of the BS4 to change, and that only at the addition points (4.0 < V_{added} <5.0 mL) of ABPHP the values are visually similar with a variation of *I* of (0.6 < *I* < 0.7 mol L^{-1}). However, when one-way ANOVA test is applied to these data sets, it is noted that they are not statistically similar, $F_{calculated}$ > $F_{critical}$ (695.31 > 4.49), total degrees of freedom = 17 and *p-value* (1.30 x 10^{-14}) is less than 0.05 (error at 95% of significance level), i.e., all are statistically different considering the metrological rigor to accept measurements and their dispersion by repeatability. This indicates that the variation of *I*, considering the dilution of the system, affects the measurement of the pH.

4 CONCLUSION

On considering a metrological study of the procedure and exploring the systems using statistical tools, it is noted that *I* of the evaluated systems considerably alters the pH of the medium and consequently modifies the equilibria studied (12 and 13). The proposition of a reference solution (BS4 with *I* = 1.0 mol L^{-1}) is valid, since we can see the strong influence of *I*. The estimate is of fundamental importance to add confidence in the results obtained, especially considering the risk of health damage resulting from the food in question. It is concluded that the values of pH measurements for systems with *I* > 0.2 mol L^{-1} in BS4 vary exponentially, there being indications that for ABPHP the quality

control using potentiometric measurements does not guarantee that the values obtained are real.

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