XX IMEKO World Congress
Metrology for Green Growth
September 9–14, 2012, Busan, Republic of Korea

DETERMINATION OF pH VALUES FOR REFERENCE POTASSIUM HYDROGEN PHTHALATE BUFFER IN WATER-ETHANOL MIXTURE (MASS FRACTION 50 %)

D. Stoica [1]*, P. Spitzer*[2]*, F.B. Gonzaga*[3]*, I. Maksimov*[4]*, P. Fisicaro*[1]*, B. Adel*[2]*, I.C. Fraga*[3]*, T. Asakai*[4]*, P.P Borges*[3]*, A Hioki*[4]

[1] Laboratoire National de Métrologie et d'Essais (LNE), 1 Rue Gaston Boissier, 75015, Paris, France, daniela.stoica@lne.fr
[2] Physikalisch-Technische Bundesanstalt (PTB), 38116 Braunschweig, Germany, petra.spitzer@ptb.de
[3] Instituto Nacional de Metrologia, Qualidade e Technologia (INMETRO), Av. Nossa Senhora das Graças, 50, Prédio 4 CEP 25.250-020, Xerém - Duque de Caxias –RJ, Brazil, fbgonzaga@inmetro.gov.br
[4] National Metrology Institute of Japan (NMIJ), Tsukuba Central 3, 1-1-1, Umezono, Tsukuba, Ibaraki 305-8563, Japan, Maksimov.Igor@aist.go.jp

Abstract: Currently, the metrological traceability of pH measurements for bioethanol is not ensured due to the lack of ethanol based reference buffer solutions. This situation leads users to calibrate their pH-electrode by means of aqueous buffer solutions, creating serious problems of reliability of measurement results. The potassium hydrogen phthalate (KHPh) solution with molality 0.05 mol·kg^{-1} was studied as a possible primary buffer in water-ethanol mixture (mass fraction 50 %). The study was carried out in the temperature range from 15 °C to 35 °C.

For this purpose, the potentiometric method based on the Harned cell (cell without liquid junction) typically employed for the characterisation of primary dilute aqueous buffer solutions has been used. In order to assess the comparability of primary pH values on KHPh buffer, the results obtained by four NMIs (National Metrology Institutes) will be presented.

Keywords: Standard potential, water-ethanol mixture, primary pH measurements

1. INTRODUCTION

The pH is one of the relevant quality parameters used to determine the corrosion potential of the bioethanol. In this media, acid-base reactions are more complex than in pure water and many efforts have been made to define primary standards [1-5]. For bioethanol, achieving the traceability must face some drawbacks. Firstly, there are some questions about the concept and the definition of pH itself. Considering the mixture as a continuous solvent, the definition of pH is conceptually similar to that for aqueous solution [6]. The pH of ethanol often called pHe is a value measured in the completely different scale from that for aqueous solutions. However, due to the low dielectric constant of pure ethanol and the dehydration of the glass electrode which is designed for measurement in water, the electrode potential is more vulnerable and depends on many experimental conditions, such as stirring rate, depth of electrode immersion, measurement time etc. Also, for water-ethanol mixtures containing a mass fraction (noted hereafter *w*) of water higher than 30 % large measurement uncertainty due to high residual liquid junction potentials has to be considered if the pH electrodes are calibrated using aqueous pH buffers [7, 8]. The wide variety of possible solvent associations adds an additional difficulty in achieving traceability to the pH of primary buffer solutions. Therefore, a suitable pH buffer must be selected with caution. The 0.05 mol·kg^{-1} potassium hydrogen phthalate is one of seven primary pH standards in aqueous solutions [1].

According to K. Izutsu et al. [9], KHPh conserves its buffer capacity in protic solvents. Thus, KHPh buffer is expected to be quite promising as standard in water-ethanol media.

The presence of the ethanol in the mixture acts on the solvation properties of the solvent, which leads to an alteration of the buffer characteristics such as the dissociation constant (pK). As a primary pH measurement procedure for aqueous solutions, the individual activity coefficient of chloride ions at the ionic strength of the buffer has to be estimated. KHPh is a weak acid, thus for the ionic strength calculation, the preliminary knowledge of dissociation constants, pK_1 and pK_2, of o-phthalic acid is required.

2. METHOD OF MEASUREMENT

pH measurements of potassium hydrogen phthalate (KHPh) of 0.05 mol·kg^{-1} in a water-ethanol (w = 50 %) mixture were carried out between 15 °C and 35 °C, in ascending order of temperatures. In the present paper the given mass fraction refers to ethanol. The studied temperatures were 15 °C, 25 °C and 35 °C, for which the hydroalcoholic mixture is characterised by the constants required for pH calculations: e.g. dielectric constant, vapour pressure, density, etc. The water-ethanol (w = 50 %) mixture is considered as a continuous solvent environment.

As for dilute aqueous solutions, the primary pH measurement method involves several steps: (1) an extrathermodynamic assumption of the individual activity coefficient of the chloride ions, (2) an experimental determination of the standard potential of the Ag/AgCl reference electrode in water-ethanol (*w* = 50 %) mixture and (3) the pH determination in the hydroalcoholic mixture of interest.

(1) In water, the ion activity coefficient (γ_i) is defined according to the Debye-Hückel equation [1]:

$$\log \gamma_{\mathrm{i}} = -Az_{\mathrm{i}}^2 \frac{\sqrt{I}}{1 + a_0 B \sqrt{I}} \qquad (1)$$

where *A* and *B* are the Debye-Hückel temperature dependent constants, a_0 is the ion size parameter interpreting mean distance between ions in electrolyte and *I* the ionic strength of the solution on molality basis.

For all hydro-organic media, the product a_0B in eq (1) is "normalised" by taking into account the properties of the mixture. This implies the next correlation [5]:

$$a_0 B = 1.5 \left(\frac{\varepsilon^{\text{water}} \rho^{\text{mixture}}}{\varepsilon^{\text{mixture}} \rho^{\text{water}}} \right)_T^{1/2} \qquad (2)$$

defined at each measurement temperature *T* with *ε* and *ρ* being the dielectric constant and the density respectively. The superscript represents the solvent to which the constant is related.

This approach is known as the modified Bates-Guggenheim convention. In this way, the continuity from pure water to a solvent mixture is ensured.

(2) The determination of the standard potential of the Ag/AgCl reference electrode (*E*°) is based on the Nernst equation (eq. (3)):

$$E = E^0 - \frac{2RT}{F} \cdot \ln\left(\frac{m}{m^0} \cdot \gamma_{\pm} \right) \qquad (3)$$

Where *E* is the measured cell potential (p_{H2} = 1 atm) of the following cell:

Pt | H_2(g) | HCl (0.01 mol·kg^{-1}) + water-ethanol (*w* = 50 %) mixture | AgCl | Ag.

R, *T* and *F* are the molar gas constant, the temperature and the Faraday constant, respectively, *m* is the amount content of HCl in hydroalcoholic solvent and m^0 represents the standard state condition (m^0 = 1 mol·kg^{-1}) in the water-ethanol (*w* = 50 %) mixture. The mean activity coefficient ($\gamma_{\pm}$) of HCl is related to the individual ionic activity coefficient by using the MacInnes approach:

$$\gamma_{\pm HCl} = \gamma_{H^+} = \gamma_{Cl^-} \qquad (4)$$

(3) The relationship used for pH calculations is given below:

$$\mathrm{pH} = -\log(a_{\mathrm{H}}) = \lim_{m_{Cl} \to 0} \left\{ \left(\frac{E - E^0}{\frac{RT}{F} \ln(10)} \right) + \log(\frac{m_{\mathrm{Cl}}}{m_0}) \right\} + \log(\gamma_{Cl}) = pa^0 + \log(\gamma_{Cl}) \qquad (5)$$

Where a_{H} is the activity of hydrogen ions in the water-ethanol (*w* = 50 %) mixture, *E* is the measured potential difference (corrected to 1atm partial pressure of hydrogen) of the following electrochemical cell:

Pt | H_2(g) | NaCl (*m*) + KHPh (0.05 mol·kg^{-1}) + water-ethanol (*w* = 50 %) mixture | AgCl | Ag.

E^0 is the standard potential of reference electrode, γ_{Cl} is the limiting (trace) activity coefficient of chloride ions (defined according to eq (1) at the ionic strength, *I*, of the buffer), and m_{Cl} is the molality of added chloride salt. As in the water medium, chloride ions at known molalities must be added to the previously prepared 0.05 mol·kg^{-1} KHPh buffer solution, in order to enable the use of the Ag/AgCl reference electrode. Fit for purpose NaCl salt has been used and NaCl solutions with molality, *m*, in the range 0.005 mol·kg^{-1} to 0.02 mol·kg^{-1} have been prepared. For each NaCl molality, *m*, a corresponding acidity function, p*a* value can be calculated.

The desired pa^0 value, required in eq (5), was obtained by linear extrapolation of p*a*, using the least squares method according to eq (6).

$$\mathrm{p}a = \mathrm{p}a^0 + \mathrm{b}m_{\mathrm{Cl}} \qquad (6)$$

where *b* is the empirical temperature-dependent constant.

Each NMI has made the extrapolation of acidity functions through at least 10 points.

3. RESULTS

The aim of this work is to validate the procedure proposed for the primary pH determination of KHPh buffer (0.05 mol·kg^{-1}) in water-ethanol (*w* = 50 %) mixture through a comparison of measurement results issued from four NMIs: INMETRO (Instituto Nacional de Metrologia, Qualidade e Technologia - Brazil), LNE (Laboratoire National de Métrologie et d'Essais - France), NMIJ (National Metrology Institute of Japan), PTB (Physikalisch Technische Bundesanstalt - Germany).

The measurements have been carried out in a matrix composed by water and commercial ethanol.

1. Measurement of *E*° in water-ethanol (*w* = 50 %) mixture

Figure 1 shows the comparison of standard potential (*E*°) of Ag/AgCl electrodes in water-ethanol (*w* = 50 %) mixture obtained by the four NMIs at 25 °C.

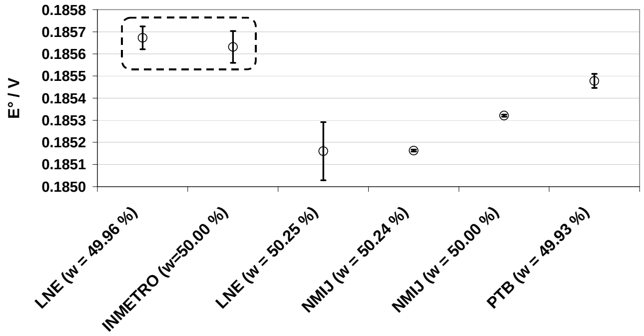

Figure 1: Comparison of standard potential (*E*°) of Ag/AgCl electrode in water-ethanol (*w* = 50 %) mixture obtained by INMETRO, LNE, NMIJ and PTB at 25 °C. The particularity of the values framed by the rectangle is explained in the text.

The HCl solution to measure the standard potential of Ag/AgCl electrodes was prepared by two ways:

The first method involves the dilution of a hydroalcoholic (w = 50 % of ethanol) HCl stock solution at about 0.1 $\text{mol}\cdot\text{kg}^{-1}$ to exactly 0.01 $\text{mol}\cdot\text{kg}^{-1}$. The data obtained with this method are enclosed by a rectangle in Figure 1. For the second method the hydroalcoholic solution is prepared starting from an aqueous HCl stock solution at about 0.1 $\text{mol}\cdot\text{kg}^{-1}$.

As shown in Figure 1, a satisfactory agreement can be observed for data obtained with a given preparation method and for a sample with a given specificity (same ethanol content).

Initial comparisons of E° values in water-ethanol solutions have highlighted the importance of sample handling and the impact of accuracy of solution preparation on measurement result.

Typically, E° values in hydroalcoholic mixture are smaller than those obtained in water for all studied temperatures. The medium effect is visible even for small differences in ethanol content. In order to attain the desired solvent composition, even small water impurity in the initial, nominally dry, ethanol reagent must be taken into account. Some participants purposely altered the solution composition and the deviation of mass fraction 0.25 % content resulted in the bias of 200 µV in E° value.

Karl Fischer titration and density measurement are two possible ways to assess accurate water content in the initial ethanol. These techniques should be used complementarily. Karl Fischer titration is most suitable for low water content solutions (typically <1 %). Ionic impurities are present in the water fraction of the sample. For samples with higher water content the density is therefore a useful parameter. The OIML R22 recommendation provides the tabulated reference values for the density of water-ethanol mixture as a function of ethanol content and temperature.

The E° values obtained with the first preparation method starting from the hydroalcoholic HCl stock solution are higher than those obtained starting from the aqueous HCl stock solution. The difference can be explained by a possible ethanol evaporation phenomenon due to long-time handling of the hydroalcoholic solution. Consequently, in this case the real ethanol content would be different from targeted value.

In Figure 1 each point is the mean of results obtained by measurements in six Harned cells in parallel in one run. As a preliminary estimation of homogeneity of electrodes used by each NMI, only the standard deviation (SD) of their potentials was taken into account.

The electrodes characteristics are similar to the one in aqueous solution.

2. Determination of pHe values of KHPh (0.05 $\text{mol}\cdot\text{kg}^{-1}$) in water-ethanol ($w$ = 50 %) mixture

The pHe values have been calculated using the eq (5). The ionic strength of the buffer required for calculating the limiting activity coefficient has been taken from [10].

In Figure 2 the pHe values for KHPh buffer of molality 0.05 $\text{mol}\cdot\text{kg}^{-1}$ in water-ethanol (w = 50 %) mixture are plotted as a function of the temperature. Moreover, the experimental pHe values at each measurement temperature are mean values calculated from the results obtained by the participants.

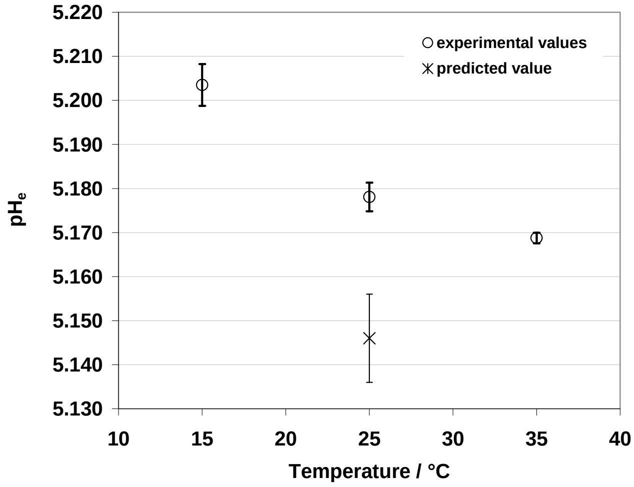

Figure 2: Temperature dependence of the pHe of KHPh buffer (0.05 $\text{mol}\cdot\text{kg}^{-1}$) in water-ethanol (w = 50 %) mixture. Each value represents the mean obtained by the participants. The half of bar of each datum represents *SD* of the mean. The point (x) at temperature 25 °C represents the predicted pH value calculated from [2].

Taken into account more high value of autoprotolysis constant of ethanol in comparison with water, the experimentally obtained pHe values of KHPh in water-ethanol mixture (w = 50 %) are higher than similar pH for aqueous solutions. According to IUPAC 2002 Recommendations [1], the nominal pH values of standard primary KHPh aqueous buffer (0.05 $\text{mol}\cdot\text{kg}^{-1}$) are 3.998, 4.005 and 4.018 at 15 °C, 25 °C and 35 °C respectively. The typical uncertainty of the primary pH values in aqueous solutions is between 0.002 and 0.005 pH (k=2).

At 25 °C, for example, the presence in the solvent of a mass fraction of ethanol equal to 50 % results in a change of pH of about 1.17 compared to the aqueous solution. This difference also called “alcohol error” can be explained by an ionisation occurring more easily in water than in hydroalcohol media. The “alcohol error” decreases with increasing temperature.

In aqueous solutions, the pH of KHPh buffer increases with the rise of temperature, while in water-ethanol (w = 50 %) medium an opposite behaviour was observed. For aqueous solutions, the temperature dependency of pH is similar to those of the pK of o-phthalic acid. White et al. [10] showed that in a water-ethanol mixture (w = 50 %) the pK of o-phthalic acid decreases as the temperature increases from – 10 °C to 25 °C. Further decrease of pK values is expected with increasing temperature, which could explain the particular characteristics of the pHe of KHPh in water-ethanol (w = 50 %) solvent.

Experimentally it is more difficult to determine the pHe in hydro-alcoholic mixtures than in water due to the possible

solvent associations which have to be taken into account. Therefore, as an option, predictive equations capable to estimate pHe values of KHPh at 0.05 mol·kg^{-1} of different ethanol content has been developed. The predictive equation given in [2] results from applying a multi-regression analysis procedure for the data obtained for five different alcohol-water mixtures at 25 °C. The difference between the experimental pHe value obtained in hydroalcoholic solvent and the predicted one is about 0.03 pH as shown in Figure 2. Figure 3 shows the comparison between the individual pHe values on KHPh buffer (0.05 mol·kg^{-1}) in water-ethanol (w = 50 %) mixture obtained at 25 °C by LNE, NMIJ and PTB, which used the same protocol for E° measurements.
For preliminary considerations, each value has associated only with the uncertainty resulting from the extrapolation of the acidity function to zero chloride molality. This is one of the main contribution to the overall pH uncertainty.

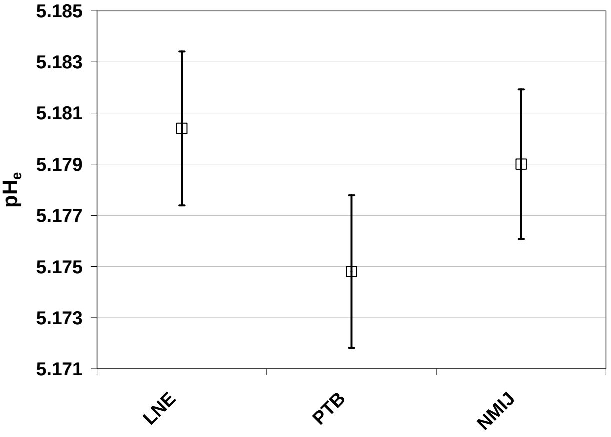

Figure 3: Individual pHe results on KHPh buffer (0.05 mol·kg^{-1}) in water-ethanol (w = 50 %) mixture. Data reported by LNE, NMIJ and PTB at 25 °C. Each bar indicates the expanded uncertainty (k =2).

Considering that the three laboratories prepared their own solution, the consistency of pHe values in water-ethanol (w = 50 %) mixture is fairly good.

Conclusions

This work can be seen as a contribution to IUPAC efforts in the standardisation of pH measurements in hydro-organic mixtures. The results obtained in the present preliminary study demonstrate the possibility to standardise primary KHPh reference buffer (0.05 mol·kg^{-1}) in water-ethanol (w = 50 %) mixture with confidence. It has been emphasised that it is important to harmonise the solution handling and measurement protocol prior to pH measurement. Main parameters affecting the $E°$ and pHe values have been identified.

Acknowledgements

The research at LNE and PTB leading to these results has received funding from the European Union on the basis of Decision No 912/2009/EC.

References:

[1] R.P. Buck et al, “Measurement of pH. Definition, standards and procedures”, Pure Appl. Chem., Vol. 74, No. 11, pp. 2169-2200, 2002

[2] S. Rondinini, P.R. Mussini, T. Mussini, A. Vertova, “pH measurements in non-aqueous and mixed solvents: predicting pH(PS) of potassium hydrogen phthalate for alcohol-water mixtures”, Pure Appl. Chem., Vol. 70, No. 7, pp. 1419-1422, 1988

[3] S. Rondinini, P.R. Mussini, T. Mussini, ‘‘Reference value standards and primary standards for pH measurements in organic solvents and water+organic solvent mixtures of moderate to high permittivities”, Pure Appl. Chem., Vol. 59, No. 11, pp. 1549-1560, 1987

[4] S. Rondinini, P. Longhi, P.R. Mussini, T. Mussini, ”Autoprotolysis constants in nonaqueous solvents and aqueous organic solvent mixtures” , Pure Appl. Chem., Vol. 59, No. 12, pp. 1693-1702, 1987

[5] S. Rondinini, “pH measurements in non-aqueous and aqueous-organic solvents: definition and standard procedures”, Analytical and Bioanalytical Chemistry, Vol. 374, No. 5, pp. 813-816, 2002

[6] K. Isutzu, “Electrochemistry in non-aqueous solutions”, Wiley-VCH Verlag GmbH&Co, Germany, Ch. 3, pp. 76, 2002

[7] P. Spitzer, P. Fisicaro,S. Seitz, R. Champion, “pH and electrolytic conductivity as parameters to characterize bioethanol”, Accred Qual Assur, Vol. 14, No. 12, pp. 671-676, 2009

[8] R.J.C. Brown, A.C. Keates, P.J. Brewer, “Sensitivities of a standard test method for the determination of the pHe of bioethanol and suggestion for improvement”, Sensors, 10, 9982-9993; doi:10.3390/s101109982, 2010

[9] K. Izutsu, H. Yamamoto, “Applicability of 0.05 mol·kg^{-1} potassium hydrogen phthalate as reference value pH standard in water-organic solvent mixtures”, Talanta, Vol. 47, pp. 1157-1163, 1998

[10] D.R. White, N.A. Harris, J.P. Rife, “First dissociation constant of o-phthalic acid and standard pH values for 0.05 m potassium hydrogen phthalate in 50 wt% ethanol/water solvent from 25 to –10°C”, J. Chem. Eng. Data, Vol. 34, pp. 347-350, 1989