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pH Measurements in diluted H_3PO_4 solutions by potentiometric method at imposed current intensity

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Abstract

The potential values of the devise constituted by two paste electrodes: ferrocene and orthochloranil at fixed current potentiometry were determined in diluted phosphoric acid solutions (0.001 - 0.1M). A new pHi is defined. Values obtained are in good agreement with those obtained with glass electrode.

Keywords: pH; Ferrocene, Orthochloaranil, Potentiometry, Phosphoric acid.

1. Introduction

Acidity functions measure the acidity level of any solvent which linked to its ability to donate protons to (or accept protons from) a solute (Brönsted acidity). The concentration of hydrogen ions in solution is also an extremely important indicator and control parameter for chemical reactions, especially biochemical reactions. The concentration of is regarded by Sorenson as:

$$C_{H^+} = 10^{-p} \tag{1}$$

Where p, the initial letter of the words Potenz, puissance, and power was called the hydrogen ion exponent by Sorensen and was called pH. This definition is firstly linked to the concentration of hydrogen ion:

$$p_aH = -\log C_{H^+} \tag{2}$$

The pH scale is by far the most commonly used acidity function, and is ideal for dilute aqueous solutions [1].

Sorensen (1909) [2] first defined the pH scale using the cell:

Pt; H2, Soln.X | Salt bridge | 0.1N Calomel electrode (3)

where vertical lines represent liquid-liquid boundaries [3].

E° is the standard potential of the calomel electrode. At each boundary; a junction potential, E_j, is created when the nature or concentration of the solutions change to either side of the barrier. The necessary condition for the measured pH to fall on the scale defined by the activity standards is that E° + E_j remain unchanged from one solution to other.

An exact determination of pH would require the introduction of hydrogen activity to pass from p_cH to p_aH:

$$p_aH = \frac{E \quad - \quad (E^\circ + E_j)}{0.059} \tag{4}$$

The development of the versatile glass electrodes has been responsible for widespread application of pH measurements in the control of industrial and commercial processes as well as in research. The discovery of the glass electrode by Max Cremer was possible because of the advances made in the nineteenth century in understanding the electrical properties of glass [4]. The increase of the studies of electrical potential permitted to Hugues to publish the results of his comparison of the glass and hydrogen electrodes in 1922 [5] and MacInnes and Doles to purpose the use of glass electrode [6]. Dole edited in 1941 his book on the glass electrodes [7]. This later received more and more attention as an alternative electrode to replace the hydrogen electrode as universal electrode but not practical due to some disadvantages. In other words, the SHE consists of a platinum electrode immersed in a solution with a hydrogen ion concentration of 1.00M. The platinum electrode is made of a small square of platinum foil, which is platinized with a finely divided layer of platinum (known as platinum black). Hydrogen gas, at a pressure of 1 atmosphere, is bubbled around the platinum electrode. The platinum black serves as a large surface area for the reaction to take place, and the stream of hydrogen keeps the solution saturated at the electrode site with respect to the gas [8].

It is interesting to note that even though the SHE is the universal reference standard, it exists only as a theoretical electrode which scientists use as the definition of an arbitrary reference electrode with a half-cell potential of 0.00 volts. (Because half-cell potentials cannot be measured, this is the perfect electrode to allow scientists to perform theoretical research calculations). The reason this electrode cannot be manufactured is due to the fact that no solution can be prepared that yields a hydrogen ion activity of 1.00M. The glass electrode is designed to determine the pH of the solutions dilute concentrations, but when the acid concentration increases two risks may induce errors:

1- The junction potential created at the reference electrode,
2- The external layer may be damaged by the concentrated acid solution.

Near pH, other acidity functions have been proposed for concentrated acid solutions, most notably the Hammett, H_o and Strehlow, $R_o(H)$, acidity functions. H_o measure the degree of protonation of an indicator colorimetrically [9] and $R_o(H)$, consists to measure the potential of the H+/H_2 couple versus that of the Ferricinium/Ferrocene (Fc^+/Fc) couple, which following Strehlow assumption, can be considered as independent of solvent [10]. Similar acidity function, named $R_i(H)$, was proposed successfully. Results obtained in concentrated mineral acids as H_3PO_4, HCl, H_2SO_4, $HClO_4$, [11-14] by the electrochemical chain constituted by ferrocene Fc↓ inserted in carbon paste as a reference electrode [15] and orthochloranil in carbon paste as an indicator of H^+ ion crossed by a low current intensity have allowed to define a new acidity function, $R_i(H)$. The values obtained are quite similar to those of $R_o(H)$ in literature [11] which have incited to its application to diluted H_3PO_4.

The encouragement results obtained in concentrated phosphoric acid [11] by the electrochemical chain constituted by ferrocene Fc↓ as a reference electrode and orthochloranil crossed by a low current intensity, have incited to its application to diluted H_3PO_4. The objective of this work is to determine the pH of phosphoric acid solutions (0.001 - 0.1 M) with oQ↓ / H_3PO_4 /Fc↓ at i = 1μA. A new pH_i is defined and compared to the pH determined by the glass electrode. We show also that pHi is an extension of $R_i(H)$ in diluted H_3PO_4.

2. Experimental

Very low soluble in phosphoric acid solutions, orthochloranil (oQ) and ferrocene (Fc) are made as electrodes according to the technique of the carbon paste electrodes as described elsewhere [11-17]. The current (i = 1 μA) is obtained by a potential generator in series with R (MΩ) ohmic resistor. 85% H_3PO_4 and Bidistilled water were used for preparing the solutions. Experiments are made at 25 ± 1°C.

3. Results and Discussion

The determination of pH is based on the global reaction:

$$oQ\downarrow + 2H^+ + 2Fc\downarrow \longrightarrow oQH_2\downarrow + 2Fc^+ \quad (5)$$

where oQ↓, oQH_2↓ and Fc↓ represent the insoluble compounds of orthochloranil, hydro-orthochloranil and ferrocene in the paste electrodes, respectively. The use of potentiometric method at imposed weak current permits to measure easily the potential variation $\Delta E_i = E_Q - E_{Fc}$ (Table 1). This method is used to avoid junction potential created at the interface of usual reference electrodes.

The practical pH [3] is obtained from the following relation:

$$pH^X = pH^S + \frac{\Delta E^S - \Delta E^X}{0.059} \quad (6)$$

ΔE^X and ΔE^S are the measured potentials with glass electrode in the unknown at pH^X and the standard acid media at pH^S, respectively.

On the basis of the practical pH and ΔE_i measurements, a new pH_i may be defined according the IUPAC recommendations [18]:

$$pH_i^X = pH_i^S + \frac{\Delta E_i^S - \Delta E_i^X}{0.059} \quad (7)$$

where 0.1 M H_3PO_4 as standard solution with $pH_i^S(H) = pH_G^S(H) = 1.6$ obtained by the glass electrode.

Table 1. Comparison between pH_i and pH_G

H_3PO_4 (M)	10^{-1}	$5\ 10^{-2}$	$2\ 10^{-2}$	10^{-2}	$5\ 10^{-3}$	$2\ 10^{-3}$	10^{-3}
ΔE_i (mV)	310	297	278	265	247	222	208
pH_i	1.6	1.8	2.1	2.4	2.7	3.1	3.3
pH_G	1.6	1.8	2.1	2.3	2.6	2.9	3.2

The ΔE_i can be interpreted by the potential measured at each electrode and while:

$$\lim_{i \to 0} pH_i = pH \quad \text{and} \quad \lim_{i \to 0} \Delta E_i = \Delta E_{i=0} \tag{8}$$

We note that ΔE_i is not well-defined at concentrations below 10^{-4} M.

Figure 1 shows that a linear plot of ΔE_i vs. pH_i indicating that vs. Nernstian response occurs when an H^+-selective electrode responds according to local thermodynamic equilibrium of the reaction (5) over the studied range of H_3PO_4 concentration.

Values of pH_i show that it varies in the same way as pH_G (Table 1). Mathematics approach shows that pH_i is related to ΔE_i by the following expression with a correlation factor 0.99889:

$$\Delta E_i = 0.403 - 0.059 \, pHi \tag{9}$$

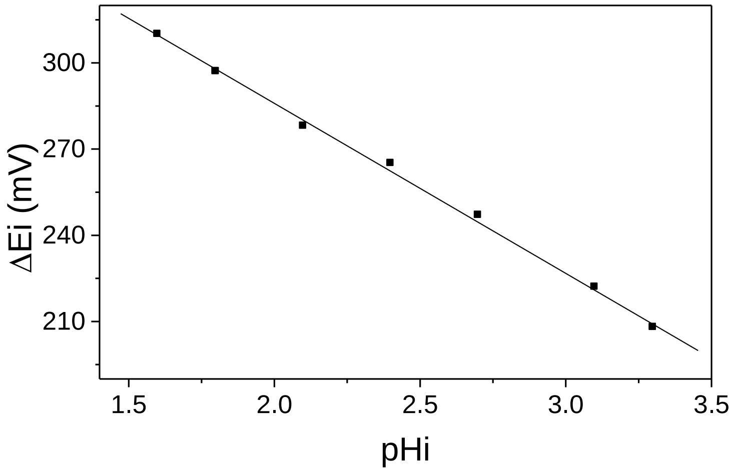

Fig.1. Variation of ΔE_i against pH_i in diluted H_3PO_4 solutions

Conclusion

The new pHi is successfully defined using the devise constituted by two paste electrodes: ferrocene and orthochloranil at fixed current potentiometry. The determined values in diluted phosphoric acid solutions (0.001 - 0.1M) are in good agreement with those obtained with glass electrode.

References

1. Rochester, C. H. (1970). *Acidity Functions.* New York: Academic Press.
2. Sorensen P.L., *Compt. Rend. Trav. Lab. Carlsberg* 8 (1909) 1.
3. Bates R.G., Determination of pH, Theory and practice, John Wiley, N.Y. Chp.2, p.20, (1964)
4. Cremer M., *Z. Biol.* 47 (1906) 562
5. Hugues W.S., *J. Am. Chem. Soc.* 44 (1922) 2860
6. D.A. MacInnes and M. Doles, *Ind. Eng. Chem., Anal. Ed.*, 1 (1929) 57
7. M. Doles, The Glass electrodes, Jihn Wiley and Sons, New York, 1941
8. Kohlmann F.J., What is pH, and how is it measured? A Technical Handbook for Industry, Chap 2, Lit. No. G004 (supercedes pH Handbook), E31.4 Printed in U.S.A. Hach Company, (2003).
9. Hammett L.P., *Chem. Rev.* 16 (1935) 67.
10. Koepp H.M., Wendt H., Strehlow H., *Z. Elektrochem.*, 64 (1960) 483.
11. Hammouti B., Oudda H., Elmaslout A., Benayada A., Bessière J., *Ber. Bunsenges. Phys. Chem.* 101 (1997) 65.
12. Hammouti B., Oudda H., El Maslout A., Benayada A., *Abhath Al-yarmouk:Basic Sci. & Eng.* 10 (2001) 273
13. Hammouti B., Oudda H., El Maslout A., Benayada A., Fresenius' J. Analyt. Chem. 365 N°4 (1999) 310
14. Hammouti B., Benayada A., El Maslout A., Oudda H., *Bull. Electrochem.* 23 (2007) 303.
15. Hammouti B., Benayada A., ElMaslout A., *Bull. Electrochem.* 13 (1997) 466.
16. Benayada A., Hammouti B., Oudda H., *J. Chem. Acta* 2 (2013) 18.
17. Benayada A., Hammouti B., Oudda H., *Phys. Chem. News*, 62 (2011) 130.
18. IUPAC, Compondium de la nomenclature en chimie analytique, Paris, 1980