2b

LIQUID JUNCTION POTENTIALS BETWEEN pH BUFFER SOLUTIONS

M.J.F. REBELO

(INIC), CECUL - R. Escola Politécnica, 58,

1294 Lisboa Codex, Portugal

Abstract

The determination of pH is a matter of prime importance in physiology as well as in many other fields. However, the assignement of a pH value to a reference solution is still a matter of controversy. The operational definition of pH includes a liquid junction potential. In order to get a better knowledge of the liquid junction contribution to the overall cell potential, measurements of the e.m.f. of cells:

Na glass electrode	Na^+ containing solution X	Bridge solution	Na^+ containing solution Y	Na glass electrode

were made.

The liquid junction is formed within a 1 mm diameter capillary tube of cylindrical symmetry in a cell vessel whose design proved to give reproducible and stable values.

1. Introduction

The operational pH is a value assigned to a solution (X) by measuring the emf of the cell (I) (1)

Portugaliæ Electrochimica Acta, 8 (1990) 61-72

$Pt|H_2|PS|Sat.\ KCl|X|H_2|Pt$ (I)

The pH of the unknown solution, pH(X), is given by

$$pH(X) = pH(PS) - \Delta E_j/k + \Delta E_j/k$$

where pH(PS) is the pH of the primary standard (PS), $k = RT(\ln 10)/F$ and $\Delta E_j = E_j(X) - E_j(PS)$, the liquid junction potential contribution to the cell emf, (ΔE), is assumed to be zero. This is effectively the same as making two separate measurements of solutions PS and X with respect to a reference electrode as recommended by IUPAC (2) with the advantage of halving the operations needed to measure the pH, and avoiding the uncertainties due to the reference electrode itself.

However, the contribution of the liquid junction potential to the operational pH value is recognized to be a source of error. Though this error is negligible for solutions having ionic strength close to that of the pH standards it is a matter of concern for other media of different ionic strength, e.g. blood plasma and other clinical media ($I = 0.16$). It has been shown (3) that pH measurements in blood plasma vs. the NBS standards may involve residual junction errors amounting to 0.03 to 0.05 pH unit.

As Durst (4) recently commented, when determining pH

values, "one is faced with two requirements, both equally difficult. The first is to evaluate or define the single ion activity coefficient; the other is to minimize and fully characterize the liquid junction potential. Both of these are classical problems; their solutions are long overdue".

In order to get a better knowledge of the liquid junction potential involved in pH measurements, cells with buffer solutions containing sodium ions and sodium glass electrodes were studied.

2. Experimental

2.1. Method

A cell vessel, which is a slight modification (1.5a,b) of a previous one developed by us to measure the operational pH of secondary standard buffers was used, Fig. 1.

Measurements were taken of the cells

Na glass electrode	Na^+ containing solution X	Na^+ containing solution Y	Na glass electrode	(II)

and

Na glass electrode	Na^+ containing solution X	Bridge solution	Na^+ containing solution S	Na glass electrode	(III)

The liquid junctions are formed within capillaries of cylindrical symmetry as described in (1). It was proved that

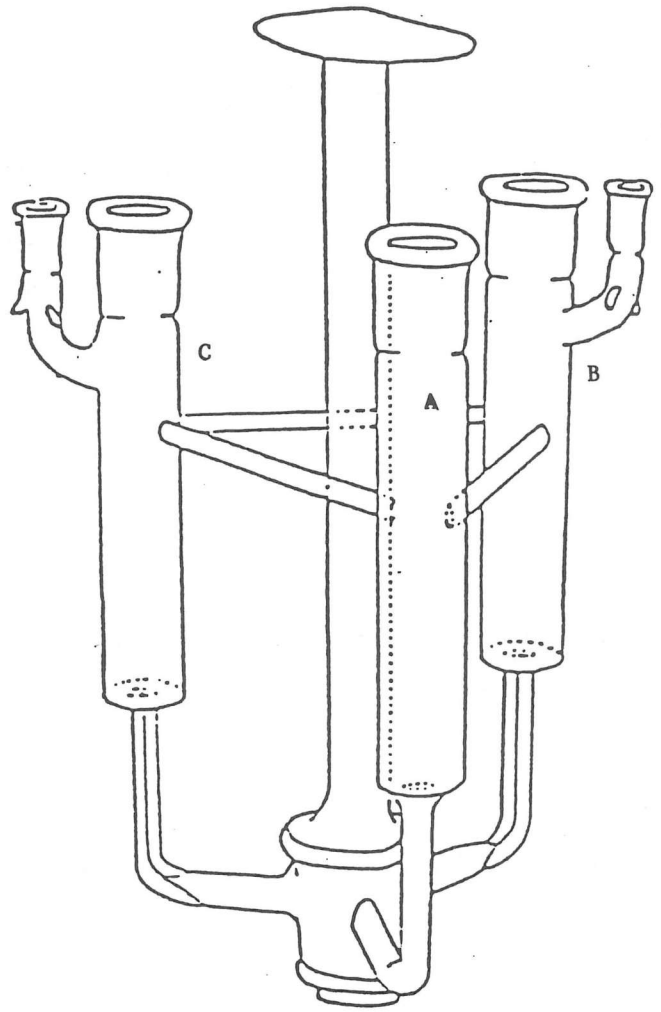

Fig. 1.

these junctions are very stable and reproducible. Cell II was made filling the compartment A with the solution having the highest density, allowing it to fill the two cappilary tubes of compartment B and C, one at a time, half way up; adding the other solution first to the other half of the capillary tubes with the aid of a needle of a hypodermic-syringe and then the rest of the compartments. In doing so the use of this cell vessel allows two cells to be made at the same time.

Cell III is prepared in a similar way but filling compartment A and the lower halves of the capillary tubes with the bridge solutions and compartments B and C with solution X and S.

2.2. Electrodes

The sodium glass electrodes used were Metrohm Zurich 60501.000 and Orion Cambridge Mass, 97-11.

The electrodes were prepared for use as recommended by the manufacturers instructions and kept in 0.1 mol dm^{-3} NaCl when not in use. The Metrohm sodium glass electrode was not used in phosphate solutions. The electrodes were always used in solutions, which had a sodium content such that pH > pNa + 4, so that interference by H^+ ion was negligible. The electrodes were calibrated frequently. Though the electrodes gave a fast response once thermal equilibrium was attained, it was observed that they were slow to reach thermal equilibrium when temperature was changed. Accordingly care

was taken to insure that enough time to reach thermal equilibrium had passed and all the solutions (rinse solution included) were preequilibrated at the required temperature.

2.3. Materials

Phosphate solutions were prepared with:

$NaH_2PO_4.2H_2O$, M.E.B. - Laboratory chemicals

Na_2HPO_4, AnalaR, BDH.

Carbonate solutions were prepared with:

$NaHCO_3$, Merck, Proanalysis

Na_2CO_3, AnalaR, BDH

Sodium chloride, Merck, Proanalysis

Potassium chloride, BDH, AnalaR

Tris(Hydroxymethyl) methylamine, BDH, Aristar

N-Tris(Hydroxymethyl) methylglycine, BDH, Biochemicals

NaOH and HCl, Merck, Titrisol 0.1.

The solutions were prepared by weight with conductivity water, redistilled from distilled water, to which potassium permanganate and sodium hydroxide were added, under a current of N_2.

2.4. Equipment

The electrodes used have a very high impedance ($\simeq$ 100-200 MΩ). Since two of these electrodes were used in the cell, it was necessary to use a differential double high

impedance input amplifier with a low input bias current to ensure that d.c. cell signals of the order of 0.1 mV could be measured accurately. It was constructed in the electronic workshop of the Department of Physics of the Faculty of Sciences of Lisbon. Low impedance leads from the amplifier were let to a Hewlett Packard 3421A data acquisition/control unit and a Hewlett Packard 85 computer. All the system was carefully grounded and a signal free from interferences was achieved.

The cells were maintained at constant temperature in a water bath thermostatized with a Julabo V thermostat.

3. Results and Discussion

Several pH buffers, having compositions close to the recommended BSI and NBS reference materials were studied. These compositions and the emf of corresponding cells (II, III) are summarized in Table I. Some modification of their compositions were made in order to meet the requirements of the system used. So, phosphate and carbonate buffers were prepared with the corresponding sodium salts in order to give the same sodium ion concentration in both buffers. The concentrations and ionic strengths are the same as BSI and NBS reference buffers. The potential differences (Table I) thus observed with cell II when these phosphate and carbonate buffers are compared is entirely due to the liquid-liquid junction potential between them, if it is assumed that γ_{Na^+} = f(ionic strength) only. The value

TABLE I. EMF/mV OF CELLS II AND III WITH LIQUID LIQUID JUNCTION FORMED WITHIN A CAPILLARY TUBE OF CYLINDRICAL SYMMETRY BETWEEN pH BUFFER SOLUTIONS (298 K)

CELL II						CELL III				
A/mol kg^{-1}	B/mol kg^{-1}	NaG	A	B	NaG	NaG	A	3.5 mol kg^{-1} KCl	B	NaG
0.025 Na_2HPO_4 0.025 NaH_2PO_4	0.025 Na_2CO_3 0.025 $NaHCO_3$			0.74				0.56		
0.05 Na_2HPO_4 0.01429 NaH_2PO_4	0.05 Tris HCl 0.01667 Tris 0.1143 NaCl			16.10				4.10		
0.05 Na_2HPO_4 0.01429 NaH_2PO_4	0.02 Na Tricine 0.06 Tricine 0.09429 NaCl			12.08				4.25		
0.05 KHPh 0.1143 NaCl	0.05 Tris HCl 0.01667 Tris 0.1143 NaCl			3.96				-1.30		

The bias potential of the electrodes were measured prior to each experiment and its value substracted from the emf readings.

One of the cells was measured seven times, the standard deviation being 0.08 mV. The other cells were set 2-3 times, the deviations being of the order of 0.1 mV.

obtained (after subtracting the bias potential of the sodium glass electrodes) is very low: 0.74 mV, and very close to that observed when a bridge of KCl 3.5 mol kg^{-1} is interposed between them: 0.56 mV. This suggests that the mobilities of the phosphate and carbonate ions match very well each other. Moreover, the use of the KCl bridge does not significantly reduce the liquid junction potential and can be dispensed with.

In order to study the behaviour of Tris buffer with the present system the composition of the buffers were chosen in such a way as to keep the sodium ion concentration, the ionic strength and the buffer components concentration as close as possible. The phosphate buffer chosen to match the above mentioned requirements was the 0.05 mol kg^{-1} Na_2HPO_4; 0.01429 mol kg^{-1} NaH_2PO_4 which has the same ionic strength and same sodium ion concentration as 0.05 mol kg^{-1} Tris HCl, 0.01667 mol kg^{-1} Tris, 0.1143 mol kg^{-1} NaCl. The phosphate buffer used, has the same composition (3.5:1) (2) as that recommended as reference standard for clinical media and the ionic strength (0.1643) similar to that of the blood.

The phthalate buffer chosen was the 0.05 mol kg^{-1} KHPh to which 0.1143 mol kg^{-1} NaCl was added. The sodium ion concentration is the same as that of the Tris buffer chosen, and the ionic strength is very close to that of the Tris buffer and blood.

The potential difference obtained for cell II is much lower when comparing this Tris buffer with phthalate

(3.96mV) than with phosphate (16.10 mV). It is even lower than the potential observed when a bridge of concentrated KCl is interposed between the phosphate and tris buffers.

These results suggest that, when comparing buffer containing uni-univalent ions with phosphate buffers, the high residual liquid-liquid junction potential is mainly due to the charge on the HPO_4^{2-} ion.

This conclusion is supported by experiments where Tris and Tricine buffers are compared directly with 0.1143 mol kg^{-1} NaCl. The liquid junction potential is also low (Table III). Table II further evidences that liquid junction potentials are additive for junctions between solutions having the same low ionic strength (≃ 0.1).

4. Conclusions

There is reasonable evidence to conclude that the mobilities of the ions HPO_4^{2-}, $H_2PO_4^-$ and CO_3^{2-}, HCO_3^- match each other very closely.

This conclusion is supported by the measured potential differences of a cell where a liquid liquid junction is formed in a capillary tube of cylindrical symmetry. This cell contains equal stoichiometric concentrations of the mono and divalent, above mentioned, ions and of sodium ions to which the electrodes (sodium glass) are reversible. The potential of the cell thus formed was 0.74 mV.

The results obtained whenever amine buffers were used, lead to the conclusion that, when using this type of

TABELA II. EMF/mV OF CELLS II AND III AT 298 AND 310 K

CELL II					CELL III				
NaG	0.0142 NaH_2PO_4 0.0500 Na_2HPO_4	NaCl 0.114	A	NaG	0.0142 NaH_2PO_4 0.0500 Na_2HPO_4	NaCl 0.114	A	NaG
	298 K		310 K		298 K		310 K	
	1.93		3.14		17.06		17.77	
	−2.37		−3.19		11.47		11.40	
NaG	0.0142 NaH_2PO_4 0.0500 Na_2HPO_4	NaCl 0.114	A	NaG				
	298 K		310 K					
	14.23		14.16					

A
0.05 Tris HCl
0.01667 Tris
0.1143 NaCl
0.02 Na Tricine
0.06 Tricine
0.0943 NaCl

All concentrations in mol kg^{-1}

See footnote on Table I.

buffers, calibrations of pH assemblies must be made against potassium hydrogen phthalate 0.05 mole kg^{-1} to which sodium chloride has been added to match the buffer ionic strength. Potassium hydrogen phthalate is to be preferred to the phosphate buffer. Furthermore liquid junction potentials are shown to be additive when the junctions are formed between solutions having the same low, ionic strength with a common cation.

References

(1) A.K. Covington, M.J.F. Rebelo, Anal. Chim. Acta, **200(1)** (1987), 245-260.

(2) A.K. Covington, R.G. Bates, R.A. Durst, Pure and Appl. Chem. (1985), **57(3)**, 531-42.

(3) R.G. Bates, Anal. Chem. **50(9)**, (1978), 1295.

(4) R.A. Durst, W.F. Kody, Y.C. Wu, Ion-Select. Elect. Rev., **9** (1987), 173-196.

(5) **a)** M.J.F. Rebelo, Ph.D. Thesis, Newcastle-upon-Tyne, 1981.

b) M.J.F. Rebelo, Port. Elect. Acta, **5**, (1987) 231-237.

(6) R.G. Bates, R.N. Roy, R.A. Robinson, Anal. Chem. **45(9)** (1973), 1663-1666.

(Received 24 April 1990
Revised form 13 July 1990)

REPORT ON THE 'IX CONGRESO IBEROAMERICANO DE ELECTROQUIMICA' (IXth IBERO-AMERICAN CONGRESS OF ELECTROCHEMISTRY)

In the week comprised between July 15th and July 21st, the 'IX Congreso Iberoamericano de Electroquimica' was held at La Laguna, Tenerife, Spain. The seat of the Congress was the Universidad de La Laguna. This Congress was a new one of a series of electrochemical meetings which were initiated in Argentina about 20 years ago. The Congress under the present edition covered all the electrochemical communities from Spanish -and Portuguese- speaking countries.

The organisation of the Congress was run by a Committee headed by Prof A. Arevalo from the University of La Laguna. The number of participants attending the Congress was 194 coming from 13 differents countries. The program consisted of 8 plenary lectures, 23 invited lectures and 225 fifteen minute presentations. Nearly 470 authors and coauthors sent communications to the Congress, the 225 communications was distributed in the following areas of electrochemistry: i) Fundamental Electrochemistry (75); ii) Electrode Materials and Electrolytes (20); iii) Electrochemical Methods of Analysis (25); iv) Molecular Electrochemistry and Bioelectrochemistry; v) Electrochemical Energy Conversion (2); vi) Corrosion, Electrodeposition and Surface Treatment (74) and vi) Industrial Electrochemistry and Electrochemical Enginneering (4). The communications were presented in four paralell sessions covering from Monday to Friday the entire day, except Wenesday afternnon, which was dedicated to an excursion to the Teide volcano.

The abstracts of the Congress were printed in a 730 pages book. The book is available at the Departamento de Quimica Fisica, Universidad de La Laguna, its price being 50 usa dollars. By the end of present year the full text of plenary and invited lectures will be published by the Secretariado de Publicaciones (Universidad de La Laguna). This book will be available at the same price as the abstract book.