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STANDARD pH VALUES FOR STANDARDIZATION OF POTENTIOMETRIC SENSORS IN 10% (w/w) ACETONITRILE–WATER MIXTURES

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Summary—Reference value standards, pH_s in 10% (w/w) acetonitrile–water solvent mixtures for 11 reference buffer solutions have been determined from reversible emf measurements of the cell Pt/Ag/AgCl/standard buffer + KCl, in acetonitrile–water/glass electrode, at 298.15 K. Values of ionization constants, required for above calculations, have been determined from reversible emf measurements of the cell Pt/Ag/AgCl/HA + A + KCl, in acetonitrile–water/glass electrode, in the same solvent composition and temperature.

Mixed aqueous organic solvents such as acetonitrile–water mixtures are widely used in DNA synthesizers, reversed-phase liquid chromatography (RPLC), capillary electrophoresis and electrochemistry. For sucessful systematic optimization of aplications in these areas, accurate pH measurements in the more widely used binary aqueous organic solvents mixtures are needed, because pH is potentially a very useful parameter for achieving and optimizing methods.[1] Nowadays, investigations into the importance of pH changes for the interpretation of the ionization effect in nonaqueous phases has been restricted by limited validity of pH measurements made with conventional electrodes calibrated in aqueous solutions.[2]

The operational cell for pH measurements in a general (aqueous, nonaqueous or aqueous-organic) solvent s is:

Reference / Salt / Sample solution at pH_x / H^+-response (A)
electrode / bridge / or Buffer Solution at pH_s / electrode
in solvent s

where, from the point of view of practical measurements, the H^+ response electrode is usually a glass electrode and is coupled with a suitable reference electrode, commonly calomel or silver–silver chloride electrode.

If E_x and E_s denote the emf measurements on the sample solution at unknown pH_x and on the standard buffer at known pH_s, respectively, and $(E_j)_x$ and $(E_j)_s$ are the corresponding liquid junction potentials localized at the liquid–liquid boundary, it can be shown that the following relation holds:

$$pH_x = pH_s + (E_s - E_x)/g + [(E_j)_x - (E_j)_s]/g \quad (1)$$

where $g = (\ln 10)RT/F$. The term $[(E_j)_x - (E_j)_s]$ is called residual liquid junction potential, and is a concealed but important factor to be controlled in terms of uncertainty in pH measurements. The IUPAC recommends to choose a standard reference solution to match pH_x as closely as possible in pH, composition and ionic strength so that the residual liquid junction potential term become small.[3] Therefore, this term is officially ignored to give:

$$pH_x = pH_s + (E_s - E_x)/g \quad (2)$$

which is the internationally recognized operational equation for the electrometric pH measurements.[3,4]

Also, when there is a well-founded suspicion that the residual junction potential term cannot be neglected (*e.g.* for possible inappropriateness or ineffectiveness of the salt bridge chosen), the error in pH_x caused can be reasonably reduced by the procedure of bracketing unknown and standards,[3,4] namely, measuring two emfs E_{s1} and E_{s2} of cell (A) with the two respective standards, pH_{s1} and pH_{s2}, one lower and the other higher than (and as close as possible to) the unknown pH_x. In such case the operational equation becomes:

$$pH_x = pH_{s1} + (E_x - E_{s1}) \times (pH_{s2} - pH_{s1})/(E_{s2} - E_{s1}) \quad (3)$$

equations (2) and (3) focus the necessity of prior knowledge of pH_s values to obtain pH_x from emf measurements in cell (A). Determination of accurate pH_s values is the key of pH-metric problem in aqueous–organic solvent mixtures and can be solved by using accepted procedures and conventions[5] quite recently endorsed by the IUPAC.

The experimental procedure for standard pH_s values determination was based on emf measurements of the reversible cell without liquid junction:[6]

$$\text{Pt/Ag/AgCl}\Big/ \begin{matrix}\text{Standard buffer + KCl}\\ \text{in acetonitrile–water}\end{matrix} \Big/ \text{Glass electrode} \qquad \textbf{(B)}$$

at 298.15 K, at fixed molality for the standard buffer but at various concentrations of KCl added to the buffer solution in acetonitrile–water mixtures. In fact, the functional expression of emf values of cell (B), E, for the evaluation of pH is:

$$p(a_{H^+}y_{Cl^-}) = pH + py_{Cl^-} = [(E^0 - E)/g] - pc_{Cl^-} \quad (4)$$

where E^0 is the standard emf of the cell, values of which are essential and have been determined as in a previous work.[7]

Equation (4) eloquently shows that the quantity $p(a_{H^+}y_{Cl^-})$, which differs from pH just by py_{Cl^-}, is determinable in exact thermodynamic terms but an extrathermodynamic assumption, *i.e.* a Debye–Hückel equation in the form that allows for the restriction of the attraction between ions due to their finite size

$$py_{Cl^-} = \frac{AI^{1/2}}{(1 + a_0BI^{1/2})} \quad (5)$$

is necessary to split the thermodynamic quantity $p(a_{H^+}y_{Cl^-})$ into the two extra thermodynamic quantities pH and py_{Cl^-}. The value of ion-size parameter a_0 in equation (5) is fixed by the Bates–Guggenheim rule

$$(a_0B)_T = 1.5[\epsilon^W\rho^S/(\epsilon^S\rho^W)]_T^{1/2} \quad (6)$$

in accordance with the IUPAC recommendations.[3,4,5] The superscripts W and S refer to pure water and to the organic mixture, respectively, and the values of the dielectric constant, ϵ, density ρ, and Debye–Hückel constant, A, are collected in a previous work.[7]

Calculation of py_{Cl^-} through equation (5) requires knowledge of the ionic strength I of the standard buffer + KCl mixed electrolyte solutions

$$I = I_S + c_{Cl^-} \quad (7)$$

but I_S, the ionic strength of the standard buffer, is, in turn, function of the H^+ concentration, c_{H^+}, which is expresed by

$$pc_{H^+} = \frac{(E^0 - E)}{g} - pc_{Cl^-} - p(y_{H^+}y_{Cl^-}) \quad (8)$$

and of the ionization constants, pK, corresponding to the equilibria involved in the standard buffer solutions in acetonitrile–water mixtures. Thus, preliminary knowledge of pK values of the pH reference materials are necessary.

Then, calculation of py_{Cl^-} values must proceed by successive iterations. Initially one takes $I = c_S + c_{Cl^-}$ and obtains py_{Cl^-} by equation (5) for their subsequent insertion in equation (8) to obtain pc_{H^+} and a better value of I by equation (7). Thus, one calculates again the py_{Cl^-} value by equation (5), and so on, until constancy of I is obtained.

Inserting py_{Cl^-} in equation (4), one distinct pH value is obtained for each concentration c_{Cl^-} examined. The standard value, pH_s, for standard buffer alone at the fixed molality recommended for International pH Standards[3] can finally be obtained as the intercept at $c_{Cl^-} = 0$ from the pH *vs* c_{Cl^-} linear regression at the mole fraction x of acetonitrile studied.

Values of the ionization constants of the pH reference materials, which are required for the iterative calculations described in the preceding paragraphs were hitherto missing. These pK values can be determined[8] from systematic measurements of the emf E of the cell C in acetonitrile–water mixtures at different concentrations of the mixed electrolyte,

$$\mathrm{Pt/Ag/AgCl}\Bigg/\begin{array}{c}\mathrm{HA+A+KCl}\\ \text{in acetonitrile–water}\end{array}\Bigg/\text{Glass electrode} \qquad \text{(C)}$$

where HA and A are the acid and basic species, respectively involved in the dissociation equilibrium studied.

Taken into account the general expression for the dissociation equilibria

$$K=\frac{c_{\mathrm{A}}y_{\mathrm{A}}c_{\mathrm{H^+}}y_{\mathrm{H^+}}}{c_{\mathrm{HA}}y_{\mathrm{HA}}} \qquad (9)$$

the functional equation (10), which permits the pK calculation is obtained

$$\frac{E^0-E}{g}+\log\frac{c_{\mathrm{HA}}y_{\mathrm{HA}}c_{\mathrm{Cl^-}}y_{\mathrm{Cl^-}}}{c_{\mathrm{A}}y_{\mathrm{A}}}=\mathrm{pK} \qquad (10)$$

If the pK value is less than 5, computation of c_{HA} and c_{A} values require the calculation of the hydrogen ion concentration, $c_{\mathrm{H^+}}$. This term must be calculated from the measured value of $p(a_{\mathrm{H^+}}y_{\mathrm{Cl^-}})$ which requires the Debye–Hückel equation and thus a knowledge of the ionic strength. Again, the use of an iterative cycle for each point of potentiometric titration at which E is measured in cell (C), must be made.

Acids with two or more equilibria, whose dissociation constants differ less than two units as tartaric and citric acids, make up a special case because it is necessary to take into account all the existing equilibria. A computer program, written in Pascal,[9] based on the minimization of the sum of the square residuals is used in order to determine these pK values.

In terms of acetonitrile–water solvent mixtures, $\mathrm{pH_s}$ data are available only for 0.05 mol/kg potassium hydrogen phtalate buffer solution[8,10] and for 0.025 mol/kg potassium dihydrogen phosphate + 0.025 mol/kg disodium hydrogen phosphate,[6] at various percentages of acetonitrile. In general, the present availability of standard buffer solution pH values, $\mathrm{pH_s}$, in mixed solvents is highly unsatisfactory and only few data for potassium hydrogen phtalate are available.[11–15] However, the lack of experimental standard $\mathrm{pH_s}$ data in 10% (w/w) acetonitrile–water mixtures prompted the determination of the standard $\mathrm{pH_s}$ values and the respective relevant pK values for 11 standard reference solutions in this widely used in RPLC solvent media.

EXPERIMENTAL

Apparatus

Values of the emf of the potentiometric cell were measured with a CRISON 2002 potentiometer (±0.1 mV) using a Radiometer G202C glass electrode and a reference Ag/AgCl electrode prepared according to the electrolytic method.[7] The cell was thermostated externally at 25 ± 0.1°C. All the potentiometric assembly was automatically controlled with a microcomputer.

Reagents

Analytical reagent grade chemicals were used unless indicated otherwise. Potassium hydrogen tartrate, potassium dihydrogen citrate, potassium dihydrogen phosphate, disodium hydrogen phosphate, sodium hydrogen carbonate, sodium carbonate anhydre, disodium tetraborate decahydrate, potassium tetraoxalate dihydrate and potassium hydrogen phthalate are Merck reagents for preparation of pH standard buffer solutions according to DIN 19266. Chemicals are dried at 110°C before use except $\mathrm{KH_3(C_2O_4)_2\cdot 2H_2O}$ which are dried below 50°C and Borax, which are keeped in a desiccator containing an aqueous solution saturated with respect to both sucrose and sodium chloride, in order to maintain the correct degree of hydration. Salicylic acid was purified by sublimation.

Stock 0.1*M* potassium hydroxide (Carlo Erba, RPE grade) solutions were prepared with an ion-exchange resin[16] to avoid carbonation and were standardized volumetrically against potassium hydrogen phthalate. All the solutions were prepared by mixing doubly distilled freshly boiled water which conductivity did not exceed 0.05 μS/cm and acetonitrile (Merck, for chromatography grade).

Procedures

Standard pH values of studied buffer solutions, in 10% (w/w) acetonitrile–water mixtures, pH$_s$, were assigned by using the procedure adopted by the IUPAC.[5] This procedure involves emf measurements of cell (B) containing the buffer solutions of specified concentration[3,5,12] with added potassium chloride.

Values of ionization constants required for the standard pH$_s$ determinations have been evaluated from titrations of acid species solutions at suitable concentration (tartaric acid, citric acid, potassium dihydrogen phosphate, boric acid, phtalic acid, salicylic acid, chloracetic acid and oxalic acid) containing approximately $5 \times 10^{-4} M$ KCl solution (in order to assure a correct electrode response) in acetonitrile–water mixtures with 10% (w/w) acetonitrile contents, using KOH solutions in the same solvent as titrant.

RESULTS AND DISCUSSION

emf measurements of cell (C) at various concentrations of acidic HA and basic A species for every buffers studied were made in 10% (w/w)

Table 1. Measured emf values of cell (C), (E) (mV), molar activity coefficients of monoprotonated species and pH and pK values at different concentrations of acidic and basic species, [HA] and [A], respectively. V_0 is the initial solution volume, V_e the equivalence volume, c_t the titrant concentration, [KCl] the initial KCl concentration and E^0 the standard emf of cell

Boric acid

V_0	V_e	C_t	[KCl]	E^0	pK$_{ap}$	
20	1.49	0.0998	6.70×10^{-4}	407.33	14.26	
V	E	[HA]	[A]	y	pH	pK$_a$
0.10	−278.5	6.93e × 10^{-3}	4.97e × 10^{-4}	0.960	8.40	9.56
0.20	−298.5	6.40e × 10^{-3}	9.88e × 10^{-4}	0.953	8.73	9.56
0.30	−311.2	5.87e × 10^{-3}	1.47e × 10^{-3}	0.948	8.94	9.57
0.40	−320.8	5.36e × 10^{-3}	1.96e × 10^{-3}	0.943	9.10	9.56
0.60	−336.4	4.34e × 10^{-3}	2.91e × 10^{-3}	0.934	9.36	9.56
0.70	−343.4	3.83e × 10^{-3}	3.37e × 10^{-3}	0.930	9.47	9.56
0.80	−350.1	3.33e × 10^{-3}	3.84e × 10^{-3}	0.927	9.58	9.55
0.90	−356.9	2.84e × 10^{-3}	4.30e × 10^{-3}	0.924	9.69	9.55
1.00	−364.0	2.35e × 10^{-3}	4.75e × 10^{-3}	0.921	9.81	9.54
						pK$_a$ = 9.55
						$s = 0.01$
						$N = 9$

Salicylic acid

V_0	V_e	C_t	[KCl]	E^0	pK$_{ap}$	
20	1.05	0.0998	7.83×10^{-4}	407.33	14.26	
V	E	[HA]	[A]	y	pH	pK$_a$
0.10	52.1	3.29×10^{-3}	1.93×10^{-3}	0.942	2.87	3.13
0.20	46.7	3.03×10^{-3}	2.16×10^{-3}	0.940	2.96	3.13
0.30	40.9	2.74×10^{-3}	2.42×10^{-3}	0.937	3.05	3.14
0.40	34.6	2.43×10^{-3}	2.70×10^{-3}	0.935	3.16	3.14
0.50	27.7	2.10×10^{-3}	3.01×10^{-3}	0.932	3.27	3.14
0.60	20.1	1.75×10^{-3}	3.34×10^{-3}	0.930	3.40	3.15
0.70	11.3	1.38×10^{-3}	3.68×10^{-3}	0.927	3.54	3.15
0.80	0.2	9.96×10^{-4}	4.04×10^{-3}	0.925	3.72	3.15
						pK$_a$ = 3.14
						$s = 0.01$
						$N = 8$

Chloracetic acid

V_0	V_e	C_t	[KCl]	E^0	pK$_{ap}$	
20	1.32	0.0998	7.83×10^{-4}	407.33	14.26	
V	E	[HA]	[A]	y	pH	pK$_a$
0.10	57.8	4.25e × 10^{-3}	2.30e × 10^{-4}	0.938	8.40	3.07
0.20	53.6	3.99e × 10^{-3}	2.53e × 10^{-4}	0.936	8.73	3.07
0.40	44.4	3.40e × 10^{-3}	3.06e × 10^{-3}	0.932	8.94	3.07
0.60	34.1	2.74e × 10^{-3}	3.66e × 10^{-3}	0.928	9.10	3.06
0.70	28.2	2.39e × 10^{-3}	3.98e × 10^{-3}	0.925	9.24	3.07
0.90	14.5	1.65e × 10^{-3}	4.66e × 10^{-3}	0.921	9.36	3.06
1.10	−5.6	8.73e × 10^{-3}	5.37e × 10^{-3}	0.917	9.47	3.06
						pK$_a$ = 3.06
						$s = 0.01$
						$N = 7$

Table 2. pK values of pH reference materials in 10% (w/w) acetonitrile–water mixtures at 298.15 K

Substance	pK_1	pK_2	pK_3
Tartaric acid	3.27 (0.02)	4.57 (0.01)	
Citric acid	3.40 (0.05)	5.01 (0.03)	6.68 (0.04)
K dihydrogenphosphate	7.46 (0.01)*		
Boric acid	9.57 (0.05)		
Phthalic acid	3.15 (0.02)	5.77 (0.04)	
Acetic acid	4.97 (0.04)		
Oxalic acid	1.49 (0.04)	4.57 (0.01)	
Chloracetic acid	3.08 (0.02)		
Salicylic acid	3.14 (0.01)		

*Value obtained from Ref. 6.

acetonitrile–water mixtures. In this paper we omit long tables giving all experimental data, but data for one series of solutions of boric, salicylic and chloracetic acids approximately $5 \times 10^{-5} M$ in 10% (w/w) acetonitrile–water mixtures are presented as example in Table 1. The pK values obtained from these measurements, using equation (10), are necessary for the subsequent pH_s values calculation and have been reported in Table 2.

The seven primary standards of the National Bureau of Standards (NBS) in aqueous media[3,17] are obviously included in this work: saturated potassium hydrogen tartrate, at 25°C (KH tartrate); potassium dihydrogen citrate, 0.05 mol/kg (KH_2 citrate); sodium hydrogen

Table 3. Measured emf values of cell (B), *E* (mV), molar activity coefficients of monoprotonated species and pH values at various KCl concentration, c_{Cl^-} (m*M*), in 10% (w/w) acetonitrile–water solutions, for all the buffers studied

Buffers	c_{Cl^-}	*E*	*y*	pH	Buffers	c_{Cl^-}	*E*	*y*	pH
Saturated potassium dihydrogen tartrate.	4.0	35.3	0.838	3.797	Potassium hydrogen phthalate 0.05 mol/kg	5.2	10.9	0.803	4.311
	11.6	63.4	0.825	3.783		15.2	38.7	0.793	4.300
	22.6	80.7	0.810	3.771		24.7	51.5	0.784	4.288
	33.0	91.5	0.799	3.746		33.6	59.9	0.777	4.276
	42.8	98.9	0.789	3.729		42.0	66.1	0.771	4.265
	49.1	102.6	0.784	3.723		53.9	73.1	0.762	4.251
Potassium dihydrogen citrate, 0.05 mol/kg	9.9	47.2	0.795	3.989	Acetic acid, 0.1 mol/l + Sodium acetate, 0.1 mol/l	7.9	−15.0	0.760	4.902
	16.2	60.1	0.789	3.981		15.4	2.2	0.755	4.901
	22.2	68.7	0.784	3.971		33.1	21.7	0.745	4.898
	28.1	74.9	0.779	3.964		43.0	28.4	0.740	4.895
	33.7	79.9	0.774	3.957		49.3	31.9	0.737	4.893
	39.1	84.0	0.770	3.950		52.3	33.5	0.736	4.892
Na hydrogen phosphate, 0.025 mol/kg + K dihydrogen phosphate, 0.025 mol/kg	3.3	−169.7	0.765	7.141	Oxalic acid 0.05 mol/kg + K hydrogen oxalate, 0.05 mol/kg	8.8	174.1	0.782	1.736
	4.7	−160.4	0.764	7.138		17.0	191.0	0.776	1.735
	5.4	−156.8	0.763	7.137		24.9	200.6	0.770	1.734
	6.1	−153.6	0.763	7.136		29.8	205.3	0.766	1.731
	8.1	−146.1	0.762	7.133		34.6	209.1	0.763	1.730
	9.5	−142.0	0.761	7.129		39.3	212.3	0.760	1.729
Na hydrogen phosphate, 0.03043 mol/kg + K dihydrogen phosphate, 0.008695 mol/kg	3.7	−199.3	0.765	7.696	Salicylic acid 0.01 mol/kg + Sodium salicylate 0.01 mol/kg	8.3	85.6	0.866	3.302
	7.4	−181.3	0.762	7.690		13.5	98.7	0.854	3.287
	14.7	−163.2	0.758	7.677		18.6	107.2	0.843	3.276
	21.8	−152.4	0.754	7.665		23.4	113.5	0.835	3.266
	32.2	−141.5	0.748	7.647		28.1	118.5	0.827	3.257
	42.4	−133.7	0.743	7.631		32.7	122.6	0.821	3.249
Sodium tetraborate 0.01 mol/kg	8.0	−289.4	0.845	9.593	Chloracetic acid 0.05 mol/l + Potassium chloracetate 0.05 mol/l	9.4	99.4	0.797	3.104
	15.6	−272.2	0.832	9.588		20.3	118.9	0.787	3.101
	23.0	−262.2	0.821	9.581		22.4	121.4	0.785	3.099
	33.6	−252.2	0.807	9.568		26.3	125.6	0.780	3.098
	40.3	−247.4	0.800	9.562		28.3	129.1	0.778	3.097
	49.9	−241.6	0.790	9.552		32.1	130.6	0.777	3.096
Na hydrogen carbonate, 0.025 mol/kg + Na carbonate 0.025 mol/kg	15.8	−374.8	0.758	11.286					
	25.6	−362.1	0.752	11.278					
	34.9	−353.9	0.747	11.270					
	43.6	−347.8	0.743	11.262					
	52.0	−343.1	0.739	11.256					
	59.9	−339.2	0.735	11.249					

Table 4. Typical regression equations of pH *vs.* chloride concentration for the reference buffer solutions in 10% (w/w) acetonitrile–water mixtures at 298.15 K

Buffer solution	Regression equation	r^2	N†
KH tartrate	$pH = 3.804 - 1.397[Cl^-]$	0.994	9
KH_2 citrate	$pH = 3.995 - 1.330[Cl^-]$	0.997	13
Phosphate buffer I	$pH = 7.150 - 4.363[Cl^-]$	0.995	11
Phosphate buffer II	$pH = 7.694 - 1.736[Cl^-]$	0.999	9
Na tetraborate	$pH = 9.602 - 0.987[Cl^-]$	0.996	15
Carbonate buffer	$pH = 11.372 - 1.889[Cl^-]$	0.991	8
KH phthalate	$pH = 4.318 - 1.229[Cl^-]$	0.999	16
Acetate buffer	$pH = 4.895 - 0.445[Cl^-]$	0.991	7
Salicylate buffer	$pH = 3.318 - 2.159[Cl^-]$	0.995	13
Chloracetate buffer	$pH = 3.108 - 0.961[Cl^-]$	0.993	9
Oxalate buffer	$pH = 1.740 - 0.288[Cl^-]$	0.993	11

†N: Number of experimental points.

phosphate 0.025 mol/kg + potassium dihydrogen phosphate, 0.025 mol/kg (phosphate buffer I); sodium hydrogen phosphate 0.03043 mol/kg + potassium dihydrogen phosphate 0.008695 mol/kg (phosphate buffer II); sodium tetraborate, 0.01 mol/kg (Na tetraborate); sodium hydrogen carbonate, 0.025 mol/kg + sodium carbonate, 0.025 mol/kg (carbonate buffer); potassium hydrogen phthalate, 0.05 mol/kg (KH phthalate). Together with other buffers considered as operational standards of pH[3,5,18] and commonly used in HPLC:[19] sodium acetate 0.1 mol/l + acetic acid 0.1 mol/l (acetate buffer); oxalic acid 0.05 mol/kg + potassium hydrogen oxalate 0.05 mol/kg (oxalate buffer); salicylic acid 0.01 mol/kg + sodium salicylate 0.01 mol/kg (salicylate buffer); chloracetic acid 0.05 mol/l + potassium chloracetate 0.05 mol/l (chloracetate buffer).

Their pH_s values are determined from emf measurements of the reversible cell without liquid junction potential, cell B, at different KCl concentrations. This fact means a high number of experimental data, but for the sake of brevity, only one series of emf measurements for each standard are quoted in Table 3, together with the corresponding molar activity coefficients values of monoprotonated species and pH.

When the pH values for each buffer solution were plotted as a function of c_{Cl^-}, straight lines of small slope were obtained. Typical regression equations are shown in Table 4 for every buffer solutions in 10% (w/w) acetonitrile–water mixtures at 10^{-3}–$10^{-2}M$ chloride concentration. The intercept at $c_{Cl^-} = 0$ give the pH_s values for each set of results, with an associated error of the order of 0.0008 in most cases, and the average pH_s values are summarized in Table 5.

Table 5. pH_s values and standard deviations of the mean for 11 standard reference solutions in 10% (w/w) acetonitrile–water mixture at 298.15 K

Reference solutions	pH_s
Saturated potassium hydrogen tartrate, at 25°C	3.802 (0.004)
Potassium dihydrogen citrate, 0.05 mol/kg	3.994 (0.007)
Sodium hydrogen phosphate, 0.025 mol/kg+ potassium dihydrogen phosphate, 0.025 mol/kg	7.149* (0.007)
Sodium hydrogen phosphate, 0.03043 mol/kg+ potassium dihydrogen phosphate, 0.0008695 mol/kg	7.697 (0.006)
Sodium tetraborate, 0.01 mol/kg	9.600 (0.003)
Sodium hydrogen carbonate, 0.025 mol/kg+ Sodium carbonate, 0.025 mol/kg	11.353 (0.05)
Potassium phthalate, 0.05 mol/kg	4.318 (0.005)
Sodium acetate, 0.1 mol/l + acetic acid 0.1 mol/l	4.898 (0.004)
Salicylic acid, 0.01 mol/kg+ sodium salicylate, 0.01 mol/kg	3.318 (0.001)
Chloracetic acid, 0.5 mol/l+ potassium chloracetate, 0.5 mol/l	3.113 (0.006)
Oxalic acid, 0.05 mol/kg+ potassium hydrogen oxalate, 0.05 mol/kg	1.744 (0.007)

*Value obtained from Ref. 6.

This table includes the standard deviation of the mean for the pH_s values. Except in the case of carbonate buffer, those values verify a very good reproducibility of measurements.

Thereby, the acetonitrile–water mixtures with 10% (w/w) acetonitrile contents have been provided of a set of 11 buffer solutions with accurately known pH_s values over the whole of pH scale in this media.

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