

δ Conversion Parameter between pH Scales (^spH and ^wpH) in Acetonitrile/Water Mixtures at Various Compositions and Temperatures

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The ^spH in acetonitrile/water mixtures at different temperatures cannot be directly measured because of the lack of calibration buffers in these hydroorganic media at most temperatures different from 25 °C. In this paper, the δ parameter has been determined for acetonitrile/water mixtures from 0 up to 90% acetonitrile at different temperatures from 15 to 60 °C, and the values were fitted to a very simple simultaneous function of composition and temperature. The δ values allow conversion of the ^wpH scale (pH measured in acetonitrile/water with electrodes calibrated in water) to the ^spH scale (pH measured in acetonitrile/water with electrodes calibrated in the same acetonitrile/water mixture). The practical determination of ^spH is direct because the calibration of the electrodes is carried out with commercial aqueous standard buffers. Thus, the ^spH value of any buffered acetonitrile/water mobile phase used in reversed-phase liquid chromatography, which is directly related to the ionized fraction of analyte and, therefore, to its average retention, can be easily known at any temperature from the measured ^wpH and the corresponding δ value.

Several analytical determinations require the proper determination of pH in organic or hydroorganic media. Specifically, in separation techniques that are performed using hydroorganic solvent mixtures, the solvent pH is one of the most relevant optimization variables. In the case of liquid chromatography, the equation describing the behavior of a monoprotic ionizable analyte retention factor (k) as a function of the pH was described as follows:^{1–3}

$$k = \frac{k_{\text{HA}} + k_{\text{A}}10^{\text{pH}-\text{p}K_{\text{a}}}}{1 + 10^{\text{pH}-\text{p}K_{\text{a}}}} \quad (1)$$

where k_{HA} and k_{A} are the retention factors of the associated and dissociated forms, respectively, $\text{p}K_{\text{a}}$ is the negative logarithmic

dissociation constant of the analyte, and the pH is that of the mobile phase. Therefore, the precise knowledge of the acid–base equilibria of common buffers and analytes in the mobile phases is necessary in order to predict their retention as a function of all the relevant variables (pH, solvent composition, and temperature). Within the useful solvent mixtures, those comprising methanol or acetonitrile in water are the most widely used to control solute retention in reversed-phase liquid chromatography. There are two main procedures for the proper measurement of the pH of these mobile phases using combined pH electrodes. One of them consists of the measurement of the pH in the mixed solvent with the electrode system calibrated in standard solutions prepared in exactly the same solvent composition as the measured solution. Then, ^spH values are obtained.^{4,5} The other one consists of measuring the pH of the hydroorganic mixture with the electrodes calibrated in pure aqueous standard buffers, ^wpH , obtaining a value in the intersolvental pH scale. In any case, the calibration and target solutions should be thermostated at the same temperature. A third possibility exists, which is often used, consisting of the measurement of the pH of the aqueous fraction of the mobile phase with electrodes calibrated in aqueous standard buffers, ^wpH , and adding the organic modifier a posteriori. This case will not be considered in this work because the measured ^wpH is not the real pH of the mobile phase^{6,7} and it is useless for calculations in hydroorganic solvents.

The ^spH scale has the ordinary physical meaning; i.e., it is equal to $-\log a_{\text{H}^+}$ in the solvent mixture used as a mobile phase. However, it requires ^spH standard values and the preparation of calibration solutions for every solvent composition and temperature to be measured, which in many cases are not available. The intersolvental pH scale (^spH) has the practical advantage of using the conventional aqueous standard buffers for the calibration, independently of the chemical nature of the organic modifier or composition of the target solution. The difference between both

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pH scales is given by the δ parameter:⁸

$$\delta = {}^s_p\text{pH} - {}^w_p\text{pH} = -\log({}^s_w\gamma_{\text{H}}^{\circ}) - \frac{\Delta E_{\text{RLJP}}}{g} \quad (2)$$

The first term on the right-most side of the two equalities is fixed by the Gibbs energy for the transference of 1 mol of protons from the standard state in water to the standard state in the organic or hydroorganic solvent at a given temperature; and the last one is the difference between the liquid junction potential (LJP) established during the calibration in the aqueous solutions and that established when measuring in the hydroorganic mixture, what is usually called residual liquid junction potential (RLJP). g is the constant that characterizes the Nernstian response and it involves the absolute temperature. Then, the difference between the pH scales is a function of the temperature since both terms of the right-most side of eq 2 are temperature dependent. The magnitude of the RLJP depends on both the internal (filling solution or salt bridge) and the external calibration and target solutions. LJP can be controlled and reduced in some extension by the choice of a well-behaved salt bridge. Salt bridges to make the electric contact between aqueous solutions have been extensively studied and the equitransference of potassium chloride in water makes this salt the most frequently used.^{9,10} In junctions between KCl saturated in water (4.8 M at 20 °C) and diluted aqueous solutions, the LJP remains approximately constant in a value of ~ 3 mV with typical variations of ± 1 mV (or 0.02 pH unit of a pH combined electrode) depending on the external electrolyte.^{4,11} The aim of the recommended multipoint procedure for the calibration of pH electrodes is not only to add more data values to the calibration curve but also to involve an average of the LJP in the different standard buffer solutions used in the calibration.^{5,12} When pH calibration and measurement operations are performed, both in aqueous solutions, the RLJP can be neglected; but this approximation does not apply when the solvents of calibration buffers and target solutions are different.^{13–15} Although RLJP between calibration in water and measurement in solvent would not be negligible, it is possible that the RLJP remains constant for determined conditions of solvent composition and temperature. In this case, the ${}^w_p\text{pH}$ values are related to the ${}^s_p\text{pH}$ through a constant δ parameter. The three conditions to be fulfilled for the validity of δ as scale converter have been established by Gelsema et al.:⁸ (1) RLJP depends on the solvents on both sides of the liquid boundary but it does not depend on the solutes; (2) RLJP does not depend on the forming device (capillary tip, ground glass sleeve, platinum wire, fritted disks, etc.); and (3) the standard potential of the glass electrode half-cell (glass membrane/internal

reference), which is in contact with the different external solutions, keeps a constant value with change of the external measuring solution. These conditions have been evaluated empirically for the specific potentiometric system that the authors were using. Although, since then, some technical modifications have been introduced in the manufacture of commercial combination pH electrodes: the aqueous KCl filling solutions, which in early times were saturated (4.8 M), have been replaced by 3.0 M KCl; different types of glass membranes, junction devices, and new patent-protected reference electrodes have appeared in the market. We expect that modern devices also fulfill the conditions for alcohol/water and for other polar solvent mixtures, but a reevaluation is required. In previous studies, δ values with modern combined electrodes in acetonitrile/water mixtures at 25 °C and also in methanol/water mixtures at different temperatures have been determined.^{16–20} Since s_pK_a values and reference ${}^s_p\text{pH}$ of solutions were available for some of these solvent compositions and temperatures, the determination of δ parameter could be achieved. This was performed in methanol/water mixtures at different temperatures, and in acetonitrile/water at 25 °C by measuring the ${}^w_p\text{pH}$ of the solutions and obtaining δ from the difference with the known ${}^s_p\text{pH}$. Different buffering substances and concentrations have been used for these works, and it was observed that for the same solvent and temperature the δ parameters obtained with different buffer solutions are consistent. Therefore, it was shown that condition 1 is fulfilled, and it could be assumed that condition 1 is also fulfilled for acetonitrile/water mixtures at temperatures different from 25 °C. Conditions 2 and 3 can be evaluated by checking the agreement between ${}^w_p\text{pH}$ values measured with various combination pH electrodes, using different junction devices, internal references, and glass membrane type.

When the s_pK_a of substances or ${}^s_p\text{pH}$ data of solutions are not available, the only option for determining δ parameter is to rely on the ${}^s_p\text{pH}$ calculated for strong acid solutions (e.g., hydrochloric acid in many solvent mixtures, which in particular were used in this work) and then to subtract it from the measured ${}^w_p\text{pH}$. Calculation of these ${}^s_p\text{pH}$ values involves the assumption of total dissociation of the strong acid in the solvent mixtures, and then, the hydrogen ion activity in the scale of same solvent is estimated as the analytical acid concentration multiplied by the activity coefficient:

$$\text{pH} = -\log \frac{m\gamma}{m^0} \quad (3)$$

m is the concentration, γ is the hydrogen ion activity coefficient, and m^0 is the unitary concentration with the same units as m . The activity coefficient can be estimated by means of the Debye–Hückel approach. This estimation method has some practical drawbacks. The first one is that the pH measurements of diluted solutions of a strong acid are less precise than those in buffered

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Table 1. Combined pH Electrode Technical Information

electrode	internal reference	filling solution	diaphragm	glass membrane type
Ross Ultra 8102	Ross	aqueous KCl 3 M	ceramic frit	GH3
Schott BlueLine 11 pH	Sylamid	aqueous KCl 3 M	platinum wire	A
Metrohm Unitrode	LL System	aqueous KCl 3 M	ground joint	U
Metrohm Solvotrode	LL System	ethanol LiCl 17 M	ground joint	T

solutions. This error can be partially compensated by fitting a large number of data in the whole range of temperature and solvent composition to get an unique and simple equation. The second one is that the use of the Debye–Hückel equation requires the knowledge of the dielectric constant and density of the solvent mixture at every composition and temperature. The lack of these data in acetonitrile/water mixtures was circumvented by the determination of dielectric constant for the complete ranges of acetonitrile composition and temperatures.²¹ In fact, the lack of dielectric constant values was the main obstacle for authors to determine $s_p\text{pH}$ standard values. Mussini et al. have measured $s_p\text{pH}$ standard values of potassium hydrogen phthalate in some acetonitrile/water mixtures at 15, 25, and 35 °C, and later, Rondinini et al. did the same in some other acetonitrile compositions, but in both cases, they were limited by the dielectric constant values available in the literature.^{22,23}

EXPERIMENTAL SECTION

Instrumentation. Potentiometric determinations were carried out with a Metrohm 702SM Titrino system, a Fischer Scientific AR25 pH-meter, and a Crison MicropH 2002 potentiometer. The volumetric additions were performed with a Metrohm Dosimat 665 autoburet controlled from a PC with the software Valora.²⁴ Solutions were thermostated by immersing into a water bath that controlled the temperature within a range of ± 0.1 °C. The used pH combined electrodes were a Schott BlueLine 11pH, Ross Ultra 8102, Metrohm Unitrode, and Metrohm Solvotrode; all of them have been designed to give accurate measurements within a temperature range from 5 to 100 °C. Technical specification of these electrodes is listed in Table 1. To avoid significant leaking through the ground glass junction, the electrodes have been filled with internal solution only up to 1 cm or less higher than the external solution.

Chemicals. Solutions were prepared with water provided by a MilliQ system, and acetonitrile by Mallinckrodt and Merck, both HPLC grade. The chemical reagents were all analytical grade or better. Combined electrodes were calibrated with commercial aqueous standard buffer solutions Crison $^w\text{pH}^{20^\circ\text{C}} = 7.00$, Crison $^w\text{pH}^{20^\circ\text{C}} = 4.01$, and Panreac $^w\text{pH}^{20^\circ\text{C}} = 2.00$ or with the aqueous standard buffers prepared by following the NBS/NIST methods: potassium hydrogen phthalate $^w\text{pH}^{20^\circ\text{C}} = 4.000$, monohydrogen phosphate/dihydrogen phosphate $^w\text{pH}^{20^\circ\text{C}} = 6.881$, and borax $^w\text{pH}^{20^\circ\text{C}} = 9.225$.⁵

Procedures. In order to compare the responses of the different combined pH electrodes, solutions 0.01 and 0.001 *m* of

hydrochloric acid and 0.05 *m* potassium hydrogen phthalate were prepared at eight acetonitrile compositions within the range from 0 to 70% by weight. Electrodes were calibrated following the multipoint procedure using three thermostated aqueous pH standard buffer solutions for each group of solutions containing the same acetonitrile composition.^{5,12} Potentials used to make the calibration curve in each set of measurements were taken as the average of the calibration potentials measured before and after the set. All the $s_w\text{pH}$ measurements were made in duplicate.

In the determination of the δ parameter, two identical systems were used. Each of them was constituted of a glass tube with a magnetic stirrer as mixing chamber, a Ross Ultra 8102 pH electrode, a Crison potentiometer, a Metrohm Dosimat autoburet, and a PC with the software Valora acquiring data and controlling the autoburet. We must note that the volumetric material and pumps in common laboratories are measuring volumes at room temperature, and so, the volumes measured experimentally and the solvent compositions reported in volume fraction scale, *v*, of this work are measured at 20 °C. The mixing chambers and the aqueous pH standard calibration solutions were thermostated at each temperature by immersion into a water bath.

The experiments consisted of sequences of successive additions of a solution from the buret into the initial volume of other solution situated into the mixing chamber. Every addition was followed by thermostating laps and a potentiometric acquisition from the pH electrode. The solution used for the initial volume and the one dispensed from the buret were of similar hydrochloric concentration but very different acetonitrile compositions. Thus, the effect of the addition steps was to change solvent composition keeping quite constant the hydrochloric acid concentration. The exact hydrochloric acid concentrations after every addition were calculated from the initial volume and concentration in the mixing chamber and the volume and concentration of the solution dispensed by the autoburet. The exact $s_p\text{pH}$ was calculated from this exact HCl concentration. The hydrochloric acid solutions have been prepared by diluting by weight a concentrated solution that was previously standardized against dried tris(hydroxymethyl)aminomethane following the standard procedures. Compositions of the hydrochloric acid solutions are shown in Table 2. In the first part, the solution of the chamber contained hydrochloric acid in pure water as solvent, and the added solution was hydrochloric acid in acetonitrile 90% v/v; thus, the potentiometric measurements range from 0 to 55% v/v acetonitrile composition. In the second part, the disposition of the solutions was at the inverse and solution in pure water was added into an initial volume of solution in acetonitrile 90% v/v, obtaining data for the acetonitrile compositions from 90 to 35% v/v. The complete curve can be constructed with the data of both parts, overlapping values in the intermediate acetonitrile composition range from 35 to 55% v/v. The successive additions have been programmed to be of

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increasing volumes in composition steps of 2.5%. Since each part consisted of 22 additions, a complete curve for any electrode, hydrochloric concentration, and temperature consisted of 46 potentiometric measurements. To convert the measured potentials in the mixtures into $s_w\text{pH}$ values, the potentials of three thermostated aqueous pH standard buffers were measured before and after every sequence of additions. Then, the calibration potential for the sequence was taken as the averaged potential using the multipoint calibration procedure. The second identical system repeated in parallel the sequences in order to obtain true duplicates. The procedure was carried out with hydrochloric concentrations of 10^{-1} , 10^{-2} , and 10^{-3} M, and for temperatures from 15 to 60 °C in steps of 5 °C. A complete set of 2760 data of $s_w\text{pH}$ at different acetonitrile compositions and temperatures by means of electrodes calibrated 120 times in thermostated aqueous standard buffer solutions was obtained.

Data Treatment. δ values were obtained from the difference between the measured $s_w\text{pH}$ and the calculated $s_p\text{H}$. As was explained, we must assume total dissociation of the hydrochloric acid and concentration of hydrogen ions equal to the total concentration of hydrochloric acid, and then the hydrogen ion activity with its standard state in the same solvent at the same temperature can be calculated as expressed in eq 3. The hydrogen ion activity coefficient is also required and it can be calculated through the Debye–Hückel equation:

$$-\log s_s\gamma = \frac{z^2 A \sqrt{I} \rho_s}{1 + a_o B \sqrt{I}} \quad (4)$$

z is the charge of the ion, in this case unity, I is the ionic strength in molal scale, A and $a_o B$ are the parameters of the equation, and ρ_s is the density of the solvent mixture at the corresponding temperature. Assuming the Bates–Guggenheim convention, the parameters of eq 4 can be obtained.^{25–27} The parameter A can be calculated as follows:

$$A = 1824600 / (\epsilon_s T)^{3/2} \quad (5)$$

where T is the absolute temperature and ϵ_s the static dielectric constant of the solvent mixture at the corresponding temperature. The ion-size parameter $a_o B$ can be obtained from

$$a_o B = 1.5 \sqrt{\left(\frac{\epsilon_w}{\epsilon_s}\right) \left(\frac{\rho_s}{\rho_w}\right)} \quad (6)$$

where ϵ_w and ρ_w are the water dielectric constant and density at the working temperature, respectively. The ionic strength of eq 4, as well as the concentration to be multiplied with the activity coefficient obtained with this expression, is in the molal scale. For aqueous solutions, the difference between molar and molal scales is frequently neglected. However, when the solutions are prepared in other solvents, the two concentration scales can differ

Table 2. Solutions Used in the Determination of δ Parameter

solution	M_{HCl}^a , mol/L	m_{HCl} , mol/kg	acetonitrile, % w/w	acetonitrile, % v/v ^a
pH1S	0.137	0.168	86.61	89.20
pH2S	0.0126	0.0156	87.58	90.00
pH3S	0.00126	0.00156	87.58	90.00
pH1W	0.0990	0.0992	0	0
pH2W	0.00990	0.00992	0	0
pH3W	0.000990	0.000992	0	0

^a Measured at 20 °C.

significantly, depending on the density of the solvent (e.g., in pure acetonitrile at 20 °C, the molal activity is more than 20% different from the molar activity). Molal and molar activity scales are related by the following equation:

$$a_c = a_m \rho_s \quad (7)$$

indicating with the subscripts c and m , molar and molal scales, respectively. Then, the molar and molal pH scales are related through the decimal logarithm of the density. In the case of the activity coefficients, the scales are related by

$$\gamma_c = (m \rho_s / c) \gamma_m \quad (8)$$

where m and c are the molal and molar concentrations, respectively.

Since the $s_w\text{pH}$ is referred to pure water where molal and molar scales are similar (with a maximum difference of 0.02 pH unit at 100 °C), then in practice, there is a unique $s_w\text{pH}$ value, which can be converted to either a $s_p\text{H}_m$ or a $s_p\text{H}_c$ value. For these conversions, the δ_m or δ_c parameters, respectively, are necessary. These two δ parameters are related by

$$\delta_c = \delta_m + \log \rho_s \quad (9)$$

In this work, the results are presented in the molal scale. Conversion into the molar scale can be achieved by using eqs 7 and 8.

The acetonitrile/water solvent mixtures have been prepared by mass fraction (weight percentage), w , but the scales were also converted to volume fraction (volume percentage), v , and molar fraction of acetonitrile, x_{ACN} . These conversions can be done as follows:

$$x_{\text{ACN}} = \frac{1}{1 + \left(\frac{M_{\text{ACN}}}{M_{\text{W}}}\right) \left(\frac{100 - w}{w}\right)} \quad (10)$$

where $M_{\text{ACN}} = 41.05$ g/mol and $M_{\text{W}} = 18.015$ g/mol, and

$$v = \frac{100}{1 + \left(\frac{\rho_{\text{ACN}}^{20^\circ}}{\rho_{\text{W}}^{20^\circ}}\right) \left(\frac{100 - w}{w}\right)} \quad (11)$$

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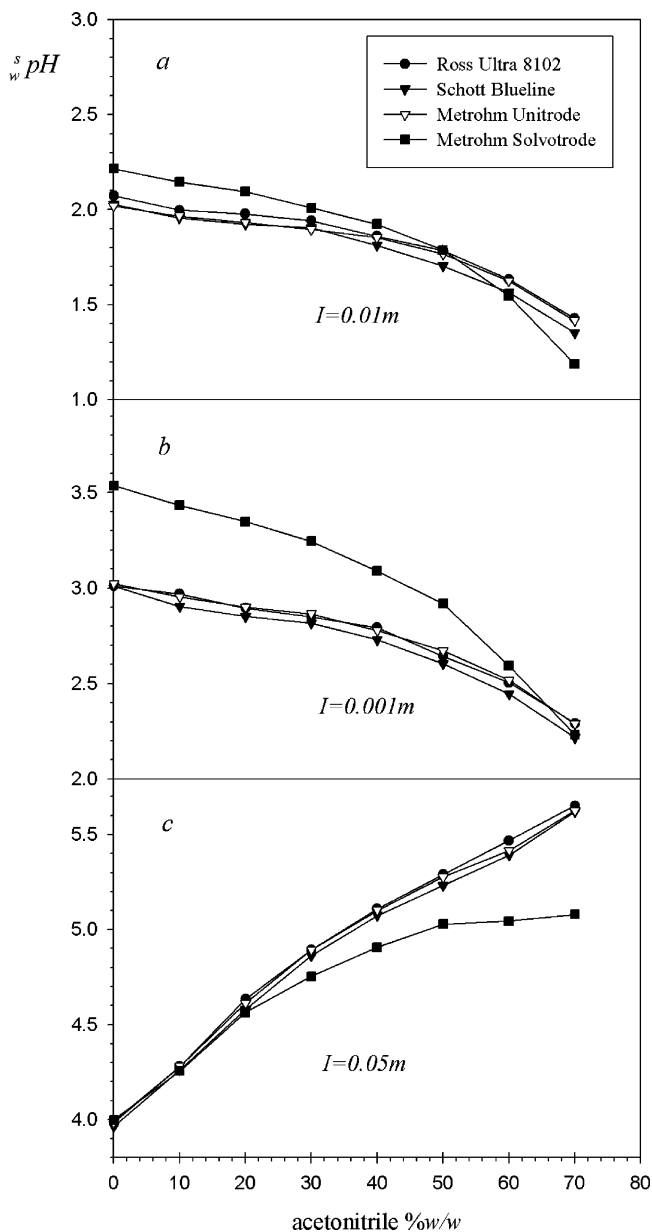


Figure 1. s_w pH values of solutions prepared in acetonitrile/water mixtures of different compositions measured with different commercial combination pH electrodes at 15 °C. Plot a, hydrochloric acid 0.01 m. Plot b, hydrochloric acid 0.001 m. Plot c, potassium hydrogen phthalate 0.05 m.

where $\rho_{\text{ACN}}^{20^\circ} = 0.78186 \text{ kg/L}$ and $\rho_w^{20^\circ} = 0.99821 \text{ kg/L}$. These densities of pure acetonitrile and pure water, respectively, have been taken from the literature.²⁸

RESULTS AND DISCUSSION

Before the accurate measurement of the δ values in acetonitrile/water mixtures, a comparison of the responses of several commercial combined pH electrodes was performed. This comparison is summarized in Figure 1. At a first glance, it is evident that the general behavior of the pH measured with the Metrohm Solvotrode electrode differs significantly from that obtained with the other electrodes.

Table 3. Parameters of Eq 12 for the Estimation of δ_m Used To Convert a Measured s_w pH Value into s_s pH_m for Different Acetonitrile Composition Scales

parameter	% w/w	% v/v ^a	x_n
a	-2.965×10^{-3} ($\pm 1.6 \times 10^{-5}$)	-2.323×10^{-3} ($\pm 1.2 \times 10^{-5}$)	-0.6779 (± 0.0036)
b	-1.971×10^{-5} ($\pm 3.4 \times 10^{-7}$)	-1.544×10^{-5} ($\pm 2.6 \times 10^{-7}$)	-4.493×10^{-3} ($\pm 7.7 \times 10^{-5}$)
c	-9.337×10^{-3} ($\pm 9.6 \times 10^{-6}$)	-9.48×10^{-3} ($\pm 7.5 \times 10^{-6}$)	-0.8488 (± 0.0022)
r^2	0.992	0.992	0.992
std dev ^b	0.023	0.023	0.023

^a Measured at 20 °C. ^b Standard deviations for δ estimated within the acetonitrile contents up to 75% w/w, 80% v/v, or 0.6 in mole fraction. For higher acetonitrile compositions, the standard deviation can be estimated as 0.05δ .

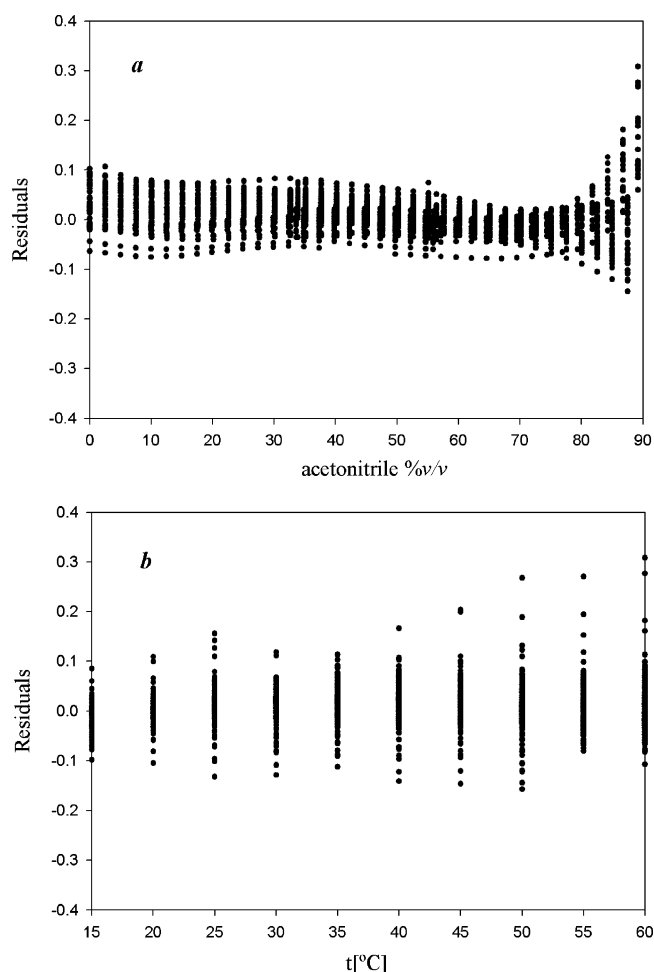


Figure 2. Residuals expressed as the difference between experimental δ_m values and the predicted by eq 12. Plot a, as a function of acetonitrile composition, and plot b, as a function of temperature.

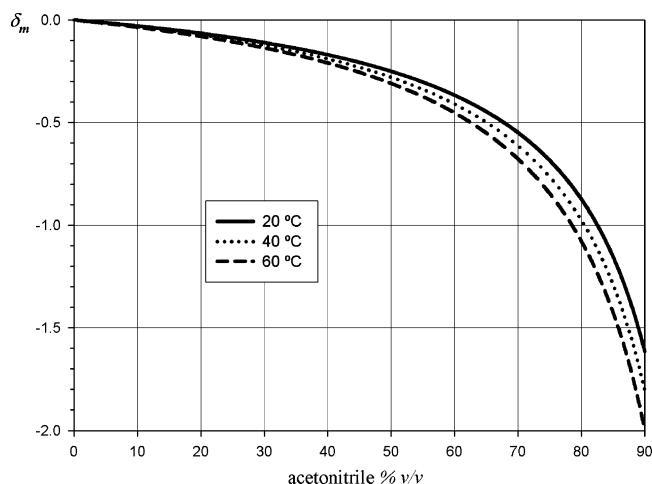
The technical specifications of the electrodes were gathered in Table 1. According to these specifications, the filling solution is the main difference between the Solvotrode electrode and the other electrodes. It contains LiCl saturated in ethanol (~17 M) as filling solution while the rest of the electrodes contains 3 M KCl in water. Thus, as expected, the RLJP of a Solvotrode electrode immersed in any aqueous solution is quite different. For the group of electrodes containing KCl as filling solution the pH values measured at 0% of acetonitrile are in close agreement (plots

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Table 4. δ_m Values for the Conversion of the ^s_wpH of Solutions in Acetonitrile/Water Mixtures at Different Temperatures Measured with pH Electrodes Containing Aqueous 3 M KCl as Filling Solutions into $^s\text{pH}_m$

acetonitrile composition		15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C
% v/v ^a	% w/w										
0	0	0	0	0	0	0	0	0	0	0	0
10	8.01	-0.028	-0.029	-0.030	-0.031	-0.032	-0.032	-0.033	-0.034	-0.035	-0.036
20	16.38	-0.063	-0.065	-0.067	-0.069	-0.071	-0.073	-0.074	-0.076	-0.078	-0.080
30	25.13	-0.107	-0.110	-0.114	-0.117	-0.120	-0.123	-0.127	-0.130	-0.133	-0.136
40	34.30	-0.165	-0.170	-0.175	-0.180	-0.184	-0.189	-0.194	-0.199	-0.204	-0.209
50	43.92	-0.243	-0.250	-0.257	-0.265	-0.272	-0.280	-0.287	-0.294	-0.302	-0.309
60	54.02	-0.355	-0.366	-0.377	-0.388	-0.398	-0.409	-0.420	-0.431	-0.441	-0.452
70	64.63	-0.532	-0.548	-0.564	-0.580	-0.596	-0.612	-0.628	-0.644	-0.660	-0.676
80	75.80	-0.846	-0.871	-0.897	-0.923	-0.948	-0.974	-0.999	-1.025	-1.050	-1.076
90	87.58	-1.566	-1.614	-1.661	-1.709	-1.756	-1.803	-1.851	-1.898	-1.945	-1.993

^a Volumes measured at 20 °C.

**Figure 3.** δ_m parameter to convert the ^s_wpH measured with combination pH electrodes containing aqueous 3 M KCl in acetonitrile/water mixtures into $^s\text{pH}_m$ (molal concentrations scale) at three different temperatures.

a, b, and c of Figure 1), indicating that the measurement is independent of other aspects involved in the design of the electrode. Furthermore, the pH values measured with the Solvotrode in the aqueous solutions depend on the external electrolyte (compare plots a, b, and c). The pH measurements obtained with this electrode at 0% acetonitrile agree with those measured with the other group of electrodes only for potassium hydrogen phthalate solution, but differ in those containing hydrochloric acid. It seems that the agreement becomes closer as the external solution concentration increases. In fact, electrodes containing LiCl saturated in ethanol as filling solution are designed for measurements in nonaqueous solutions, and they do not measure accurately the pH of aqueous solutions. Moreover, calibration of these electrodes by using aqueous standard buffers is not appropriate, and then, standard buffer solutions (with exactly known ^spH) prepared in solvents where the LiCl saturated in ethanol behaves as a good salt bridge must be required.

Other conclusions related to the RLJP can be extracted from the analysis of the electrode responses as the acetonitrile content increases. For every plot (a or b), the hydrochloric acid molal concentration at different acetonitrile compositions are the same. Thus, for the group of electrodes filled with 3 M KCl solution,

the trend with the increase of acetonitrile contents toward lower measured ^s_wpH values is similar in both plots with variations arriving to -0.7 pH units at 70% w/w. This behavior confirms the fulfillment of condition 1 (see introduction section) and thus, the constancy of δ values regardless the external solution.

The Solvotrode electrode behavior as the acetonitrile composition increases is completely different from the other electrodes; furthermore, the decrease in pH of hydrochloric acid solutions at 0.001 and 0.01 *m* measured with this electrode when the acetonitrile contents increase do not agree (plots a and b). Neglecting the logarithmic activity coefficient for this electrode, the estimated δ value is zero at 38% w/w in plot a and at 53% w/w in plot b and decreases 1 pH unit in going from water to 70% of acetonitrile in the more concentrated hydrochloric solution, while in the more diluted solution, the decrease for the same increase in acetonitrile composition is 1.3 pH units.

In the case of potassium hydrogen phthalate solutions, the plot looks different from the hydrochloric acid plots because the shifts of the ^s_wpH from the value in water is affected not only by the terms involved in the δ parameter but also by the shift of both acidity constants of phthalic acid (and the ^spH associated to the phthalate solutions) as the acetonitrile composition increases. The explanation of this behavior would require a deeper analysis, which exceeds the aim of this work. However, it is interesting to observe that, using a buffering solution, with ionic strength and pH higher than those corresponding to the hydrochloric solutions, the ^s_wpH values measured with Solvotrode, once again, do not agree with the ^s_wpH measured with electrodes containing 3 M KCl as filling solutions.

With these results, the Ross Ultra 8102 electrode was chosen as representative model of the electrodes containing 3 M KCl filling solution for δ parameter determinations. The experimental δ_m values in the acetonitrile composition range from 0 to 90% by volume and temperatures from 15 to 60 °C have been fitted to the following empirical equation:

$$\delta_m = X(a + bt)/(1 + cX) \quad (12)$$

a, *b*, and *c* are the fitting parameters, *t* is the temperature in the Celsius scale, and *X* is the acetonitrile composition, which can be expressed in different composition scales. The complete data set

Table 5. Comparison of the δ_c Determined Previously at 25 °C Using Different Buffer Solutions with the Values Calculated with Eq 12 and Converted with Eq 9 of This Work

acetonitrile % v/v ^a	δ_c^b	δ_c^c	Δ^d
10	-0.01 (± 0.02)	-0.04 (± 0.02)	-0.03
20	-0.03 (± 0.03)	-0.08 (± 0.02)	-0.05
30	-0.04 (± 0.03)	-0.14 (± 0.02)	-0.10
40	-0.14 (± 0.03)	-0.21 (± 0.02)	-0.07
50	-0.22 (± 0.09)	-0.30 (± 0.02)	-0.08
60	-0.46 (± 0.11)	-0.43 (± 0.02)	+0.03

^a Volumes measured at 20 °C. ^b Determined previously at 25 °C with different buffer substances.¹⁷ ^c Calculated in this work with eqs 9 and 12. ^d Difference between third and second columns.

Table 6. Comparison between the s_pH_m Values of Obtained from the Conversion of the $s_w pH$ Values Measured in the Solutions of Potassium Hydrogen Phthalate 0.05 m Dissolved in Acetonitrile/Water Mixtures at 15 °C by Using the δ_m and the s_pH_m Values Obtained from the Literature

acetonitrile %w/w	s_pH_m (15 °C)		
	literature	measured ^c	Δ^d
0	4.00 ^a	3.98	+0.02
10	4.34 ^{a,e}	4.30	+0.04
20	4.72 ^{a,e}	4.67	+0.05
30	4.98 ^a	4.99	-0.01
40	5.23 ^{b,e}	5.26	-0.03
50	5.46 ^b	5.51	-0.05
60	5.75 ^{b,e}	5.78	-0.03
70	6.16 ^b	6.16	0.00

^a From ref 22. ^b From ref 28. ^c Obtained from conversion of the $s_w pH$ values measured in solutions potassium hydrogen phthalate 0.05 m at 15 °C using the δ_m parameters calculated with eq 12. ^d Difference between bibliographic and measured $s_w pH$ values. ^e Interpolated values.

was first divided into three groups according to the corresponding hydrochloric concentrations (0.1, 0.01, and 0.001 m) and fitted separately. Statistic comparison of the parameters using the Fischer distribution²⁹ has been carried out, and no significant differences have been found between the parameters obtained for the three different concentrations. Additionally, the δ_m parameters estimated with the equations corresponding to the different hydrochloric concentration have been evaluated, and the values obtained do not show any trend with to the hydrochloric concentration. We conclude that δ_m values do not depend on the hydrochloric acid concentration within the measured concentration range. Hence, the complete data set was fitted to a unique equation and the best fit gave the parameters showed in Table 3. The residuals of the fittings, given as the difference between experimental and predicted values, as a function of acetonitrile contents and also as a function of temperature are shown in Figure 2. The residuals are well distributed within a constant range for low and intermediate acetonitrile contents, but there is a significant increase from acetonitrile compositions higher than 75% w/w (80%

v/v or 0.6 in mole fraction). However, within this organic solvent-rich range the magnitude of δ_m is also large (negative), and thus, the relative error is quite acceptable. Standard deviations of δ_m parameter obtained from eq 12 within the composition range from 0 to 75% w/w, 80% v/v, or 0.6 acetonitrile mole fraction are ± 0.023 and, for larger acetonitrile contents, are about $\pm 5\%$ of the estimated δ_m .

The δ_m values calculated with eq 12 for some acetonitrile compositions and temperatures are given in Table 4, and plots as a function of the acetonitrile composition for three different temperatures are shown in Figure 3. Differing from methanol/water solutions,^{8,19,20,30} in the acetonitrile/water mixtures, the δ_m values are always negatives; thus, any pH value expressed or obtained in the $s_w pH$ scale is lower than the value corresponding to the s_pH_m scale. This fact points out the importance of the proper notation of the used pH scale. The effect of temperature on δ_m is negligible for low acetonitrile contents and becomes significant as the organic solvent fraction increases, arriving to -0.1 pH unit per each 10 °C at 90% w/w acetonitrile. This dependence is expected since both terms on the right-most side of eq 2 depend on temperature, the last one explicitly in g . δ_m values obtained from eq 12 were converted into δ_c by using eq 9, and the results were compared with the values determined previously for various acetonitrile/water mixtures at 25 °C using different buffer compounds (see Table 5). The results are good, taking into account the standard deviations involved in the measurements. An indirect way to evaluate our results consists of checking the agreement between s_pH_m calculated by conversion of the $s_w pH$ values of potassium hydrogen phthalate 0.05 m solutions at 15 °C in different acetonitrile/water mixtures with those published by Mussini and Rondinini. The reported values have been measured with cells without liquid junctions (based in hydrogen and also quinhydrone electrodes).^{22,31} Calculated and literature s_pH_m values are listed in Table 6. Despite our values being obtained from conversion of values determined with another cell type, the obtained s_pH_m values are in excellent agreement with those reported.

CONCLUSIONS

Conditions for the use of a δ parameter to convert $s_w pH$ measured in acetonitrile/water mixtures with modern glass pH electrodes to s_pH have been evaluated. $s_w pH$ and the δ parameter depends on the filling solution of the electrodes and are independent of other technical specifications like glass membrane type, junction device type, and internal and external references. Then, $s_w pH$ values measured in acetonitrile/water mixtures with different glass combined electrodes are the same when the filling solution has the same composition. On the contrary, the measured $s_w pH$ value can be markedly different when the filling solution has a different composition.

An experimental procedure was developed in order to use an automatic buret to change solvent composition but with small changes in solute concentration. This system was used for the determination of the δ parameter necessary to convert any $s_w pH$ value, measured with a glass combined electrode with filling solution of aqueous 3 M KCl, into s_pH_m (in the molal scale).

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Finally, the complete δ_m data set was fitted to a very simple equation, which allows the estimation of δ_m parameter at any temperature and solvent composition. The δ_m parameter determined in this work can be used to carry out acid–base studies and pH determinations at different temperatures in acetonitrile/water mixtures using the conventional pH electrodes calibrated in the aqueous standard solutions but arriving at results in the reference scale of infinite dilution in the same solvent. Hence, the preparation of calibration solutions for every acetonitrile composition can be avoided and the lack of reference pH values for these solutions in acetonitrile/water mixtures at temperatures different than 25 °C is overcome.

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