

Assignment of reference pH-values to primary standard buffer solutions for standardization of potentiometric sensors in acetonitrile-water mixtures

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Abstract. Standard pH-values pH_{PS} for seven primary standard buffer solutions in 0, 10, 30, 40, 50, 70 and 100% (w/w) acetonitrile-water mixed solvents at 298.15 K were determined according to the criteria recently endorsed by IUPAC. The preferential solvation of the ions in acetonitrile-water mixtures was studied in order to clarify the acid-base behaviour of the solutes in such mixtures. The influence of variation in the solvent composition on pH_{PS} values was considered with a view to obtaining correlations that can be used to determine the pH_{PS} values in any acetonitrile-water mixture up to 70% (w/w) acetonitrile. The pH_{PS} values were then correlated with the weight and volume percentages and molar fraction of acetonitrile and with the Kamlet-Taft, π^* , α and β solvatochromic parameters of the acetonitrile-water mixtures. The equations obtained permit the standardization of potentiometric sensors in these mixtures.

Introduction

In several applications such as biotechnology, high-performance liquid chromatography, capillary electrophoresis and electrochemistry, pH-measurements in acetonitrile-water mixtures are of fundamental importance. Most researches have focused attention on mobile phase optimization, since this is the easiest way to control retention and selectivity in liquid chromatography (LC). Recently, the linear solvation energy relationship (LSER) based on the Kamlet Taft multiparameter scales [1, 2] was used to study retention in LC. However, this approach only allows for the prediction of retention in mobile solvent mixtures of different compositions, but provides no information about the pH of the mobile phase, which is important in understanding the retention process [3]. Studies of pH-changes aimed at interpreting the ionization effect in non-aqueous mobile phases in liquid chromatography have been restricted by the limited validity of pH-measurements made with

conventional electrodes calibrated in aqueous solutions [4].

The conclusions in a recent IUPAC document on primary standards for pH measurements in water + organic solvent mixtures [5] indicate that the present availability of standard buffer solution pH-values, pH_{PS} , is highly unsatisfactory and fresh data are required. The available data are unfortunately limited to a few typical buffers (acetate, succinate, oxalate, phosphate) in methanol-water, ethanol-water or dimethylsulphoxide-water mixtures [5]. The situation is better for the potassium hydrogen phthalate buffer, whose pH_{PS} values are known for binary aqueous mixtures with a greater variety of organic solvents [6].

However, with acetonitrile-water mixtures, the use of the hydrogen electrode is not appropriate because of its poor response in contact with acetonitrile [7, 8] and the quinhydrone electrode cannot be used as H^+ -sensing electrode in basic media [9]. Moreover for practical reasons, in most measurements a single glass electrode replaces the hydrogen electrode. The definition of the pH-scale is quite distinct from the measurement of pH with glass – reference electrode – pH meter assemblies in which several standards are used in order to take into account possible deficiencies in the electrode and meter performance [10–12].

Determination of accurate pH-values of reference primary standard buffer solutions for standardization of potentiometric sensors is the key pH-metric problem in aqueous-organic solvent mixtures such as acetonitrile-water [4, 5]. The internationally recognized operational equation is used for the electrometric pH measurements:

$$pH_x = pH_{PS} + \frac{(E_{PS} - E_x)}{k_{g1}} \quad (1)$$

$$\begin{array}{c} \text{Reference} / \text{Salt} / \text{Sample solution} / \text{Glass} \\ \text{electrode} / \text{bridge} / \text{at } pH_x \text{ or buffer} / \text{electrode} \end{array} \quad (A)$$

solution at pH_{PS}

where E_x and E_{PS} denote the emf measurements in cell A on the sample solutions at unknown pH_x and on the reference primary standard buffer solution at known pH_{PS}

respectively, and k_{gl} is the practical slope of the E vs. pH function [10, 12].

The reference pH_{PS} values of the primary standard buffer solutions depend on the nature of the solvent and in acetonitrile-water mixtures they vary with solvent composition in a manner which is not easily understood. The use of solvent mixtures permits a range of parameter values to be obtained, but this procedure introduces the added complication of the preferential solvation of the species participating in the ionization process. If a solute interacts with one of the solvents more strongly than with the other, the solute is preferentially solvated by the former solvent. The solvatochromic parameter, $E_T(30)$, proposed by Dimroth and Reichardt [13], has been used to study preferential solvation in many binary mixtures [14–16]. For acetonitrile-water mixtures, the betaine used to establish the $E_T(30)$ scale is preferentially solvated by acetonitrile in the water-rich region and by water in the acetonitrile-rich region. The solvation of this betaine may, however, be different from that of inorganic ions since it is large and hydrophobic. In water-acetonitrile mixtures, the specific solvation of iodide and chloride ions has been studied by UV and RMN, respectively [17, 18]. The results showed that these ions are preferentially solvated by water.

The quasi-lattice quasi-chemical (QLQC) theory [19–21] has been applied to quantify the preferential solvation by water of the hydrogen ions, δ_w , in acetonitrile-water mixtures. This is defined as $\delta_w = x_w^L - x_w$, the excess (or deficiency) of the local mole fraction of water, x_w^L , in the vicinity of a hydrogen ion over its mole fraction in the bulk, x_w , in a very dilute solution. The QLQC method permits the calculation of the preferential solvation parameter as a function of the composition of the solvent, on the basis of information that is independent of the transfer of the ion to the solvent mixture.

Central to the study of primary standard pH-values in organic-water mixtures is the problem of how the solute species react to changes in the solvent that forms their solvation sphere. In order to characterize this important zone of the solvent, a group of solvatochromic parameters was proposed (π^* , α and β) and they have been reported for acetonitrile-water mixtures [22–24]. π^* measures the polarity and polarizability of these solvents and α and β measure their hydrogen-bond acidity and hydrogen-bond basicity, respectively.

The present study concerns the assessment of pH-values for all seven primary standard buffer solutions in acetonitrile-water mixtures up to 70% (w/w) acetonitrile, according to the criteria recently endorsed by IUPAC for the primary standardization of pH-measurements in binary aqueous organic solvent mixtures of moderate to high permittivities [5]. The variation of the pH_{PS} values obtained over the whole composition range studied can be explained by taking into account the preferential solvation of hydrogen ions in acetonitrile-water mixtures calculated on the basis of the QLQC method. Finally, the pH_{PS} values were subjected to multiparameter correlations with π^* , α and β solvatochromic properties of the solvents. The pH_{PS} values and equations obtained allow calculation of the pH_{PS} values in any acetonitrile-water mixture up to 70% (w/w) acetonitrile, and thus permit the

standardization of potentiometric sensors in these mixtures.

Experimental

Apparatus

Values of the emf of the potentiometric cell were measured with a CRISON 2002 potentiometer (± 0.1 mV) using a Radiometer G 202 C glass electrode and a reference Ag/AgCl electrode prepared according to the electrolytic method [25] and directly immersed in the solution, to avoid the residual liquid junction potentials [26].

The glass electrode was stored in water when not in use and soaked for 15–20 min in acetonitrile-water mixture before potentiometric measurements. The stabilization criterion for the emf readings was 0.2 mV within 150 s; in all instances the electrode system gave stable and reproducible potentials within 5 min.

The reference electrode was stable for three months of continuous work. The E° -values used here are the average of at least 15 standardizations. The standardization of the electrode system was carried out each time the solvent media or electrodes were changed and the constancy of the E° -values was ensured by continual surveillance by means of periodical calibrations. The cell was thermostated externally at 25 ± 0.1 °C. The potentiometric assembly was automatically controlled with a microcomputer.

Reagents

All chemicals used were of analytical reagent grade unless otherwise indicated.

All the solutions were prepared by mixing freshly boiled, doubly distilled water and acetonitrile (Merck, for chromatography grade). The concentration of the primary standard reference solutions were chosen as recommended by IUPAC [27], Table 1. Primary standards (potassium hydrogen tartrate, potassium dihydrogen citrate, disodium hydrogen phosphate, potassium dihydrogen phosphate, sodium hydrogen carbonate, sodium carbonate, sodium tetraborate and potassium hydrogen phthalate) were Merck reagents for preparation of pH standard buffer solutions according to DIN 19266. The chemicals were dried at 110 °C before use except borax, which was kept in a desiccator containing an aqueous solution saturated with both sucrose and sodium chloride, in order to maintain the correct degree of hydration. Stock 0.1 mol/l potassium hydroxide (Carlo Erba, RPE grade) solutions were prepared with an ion-exchange resin [26] to avoid carbonation, and standardized volumetrically against potassium hydrogen phthalate.

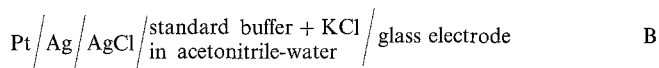
Procedures

Standard pH-values of primary buffer solutions in acetonitrile-water mixtures with 10, 30, 40, 50 and 70% (w/w) of acetonitrile, pH_{PS} , were assigned by using the procedure adopted by IUPAC [5]. This

Table 1. Primary standards reference solutions

- | |
|---|
| 1. Saturated (at 25 °C) potassium hydrogen tartrate (KH tartrate) |
| 2. 0.05 mol/kg potassium dihydrogen citrate (KH ₂ citrate) |
| 3. 0.025 mol/kg disodium hydrogen phosphate |
| 0.025 mol/kg potassium dihydrogen phosphate
(phosphate buffer I) |
| 4. 0.03043 mol/kg disodium hydrogen phosphate |
| 0.008695 mol/kg potassium dihydrogen phosphate
(phosphate buffer II) |
| 5. 0.01 mol/kg sodium tetraborate (Na tetraborate) |
| 6. 0.025 mol/kg sodium hydrogen carbonate |
| 0.025 mol/kg sodium carbonate
(carbonate buffer) |
| 7. 0.05 mol/kg potassium hydrogen phthalate (KH phthalate) |

was based on emf-measurements of the reversible cell without liquid junction:



at 298.15 K, at fixed molality for the primary standard buffer but at various concentrations of KCl added to the buffer solution in acetonitrile-water mixtures. The functional expression for the evaluation of pH is:

$$p(a_{\text{H}^+} y_{\text{Cl}^-}) = \text{pH} + p y_{\text{Cl}^-} = [(E^\circ - E)/k_{\text{gl}}] - p c_{\text{Cl}^-} \quad (2)$$

where E° is the standard emf of the cell. E° -values were determined as in a previous study [26]. The potential slope of the glass electrode, k_{gl} , is usually referred to the theoretical slope, k , used here, by the electromotive efficiency, $\alpha = k_{\text{gl}}/k$, which is independent of the individual electrodes and in water has an average value of 0.9975 [12].

Equation (2) shows that the quantity $p(a_{\text{H}^+} y_{\text{Cl}^-})$ is determinable in exact thermodynamic terms, but an extrathermodynamic assumption, i.e. a Debye-Hückel equation,

$$p y_{\text{Cl}^-} = \frac{A I^{1/2}}{(1 + a_0 B I^{1/2})} \quad (3)$$

is necessary to split the thermodynamic quantity $p(a_{\text{H}^+} y_{\text{Cl}^-})$ into the two extrathermodynamic quantities pH and $p y_{\text{Cl}^-}$.

In compliance with IUPAC rules [5, 28], the value of $a_0 B$ is assigned at the appropriate temperature T by an extension of the Bates-Guggenheim convention [5, 26] :

$$(a_0 B)_T = 1.5 [\varepsilon^W \rho^S / (\varepsilon^S \rho^W)]_T^{1/2} \quad (4)$$

where W and S refer to pure water and to the appropriate solvent mixture, respectively. Values of the dielectric constant, ε , and densities, ρ , involved in the calculation of the Debye-Hückel constants A and $a_0 B$ were taken from data in the literature [9, 29–31].

Calculation of $p y_{\text{Cl}^-}$ from Eq. (3) requires knowledge of the ionic strength I of the primary buffer + KCl mixed electrolyte solution. However I is, in turn, a function of the H^+ concentration, c_{H^+} , and of the ionization constants, pK , corresponding to the equilibria involved in the standard buffer solution in acetonitrile-water mixtures. These pK -values required were determined in previous works [32–34].

Thus, calculation of $p y_{\text{Cl}^-}$ proceeds by successive iteration [5, 28]. By inserting the $p y_{\text{Cl}^-}$ values in Eq. (2), a distinct pH-value is obtained for each concentration c_{Cl^-} examined. The standard value, pH_{PS} , for the seven primary buffers at the fixed concentrations recommended as International pH-Standards [27], Table 1, can finally be obtained as the intercept at $c_{\text{Cl}^-} = 0$ from the pH vs. c_{Cl^-} linear regression at each mole fraction x of acetonitrile studied.

Results and discussion

Emf-measurements for cell B were made at different concentrations c_{Cl^-} of KCl added to the constant concentration of each of seven primary standard buffers, Table 1, in 10, 30, 40, 50 and 70% (w/w) acetonitrile-water solvent composition. For each primary standard buffer solution, various series of measurements were performed for a total of 784 independent measurements over the solvent interval explored. As an example, several values for one series of measurements in each primary standard reference solution are given in Table 2. Phosphate buffers and Na tetraborate and carbonate buffer are not soluble in 70% (w/w) acetonitrile-water mixtures.

The statistical analysis of variance was applied to the various independent sets of measurements. The variances calculated were s_w^2 , the variance within-sets of data or series of measurements and s_b^2 , the variance between-sets

of data. If these two variances do not differ significantly by applying the F-test for a 5% level of significance, then it can be concluded that for a given primary standard buffer all the points of every data set belong to the same population and therefore it is permissible to calculate the total average, pH_{PS} , and the standard deviation, s , by fitting all the points together and carrying out least-squares analysis. If the variances differ, then the most of the error derives from the variability from one series of data to another, the pH_{PS} value is obtained by averaging the different intercepts and the total variance $s^2 = s_b^2 + s_w^2$ can be calculated.

Table 3 shows the single studied pH_{PS} values for the seven primary standard buffer solutions in 10, 30, 40, 50 and 70% (w/w) acetonitrile-water mixtures and the standard deviation values, s , together with the standard pH_{PS} values in water [35]. This table also shows the pH_{PS} values in pure acetonitrile solvent for the three primary standard buffers that are soluble in this medium. In order to obtain these values, the potentiometric system described previously [36] was used and the standard potential of the cell was determined by titration of picric acid solutions in acetonitrile with tetrabutylammonium hydroxide, as in previous studies [37, 38].

pH glass electrodes exhibit a sub-Nernstian pH-response at medium pH-values outside the acid and sodium error range [10, 12]. Taking into account the small electromotive efficiency of glass electrodes reported in aqueous solutions, $\alpha = 0.9975$ [12], and re-estimating the standard emf of the cell [26], the obtained pH_{PS} are some milliunits higher than the reported ones, but the deviation is not noticed since it is included in the standard deviation values shown in Table 3.

The smoothing single-stage multilinear regression method [30] was applied to the whole set of pH_{PS} values over the range from 0 to 70% (w/w) acetonitrile at 298.15 K in order to check the internal consistency of the results obtained. In this case, if the usual concentration by volume $\%(v/v)$, v , or by weight $\%(w/w)$, w , and the molar fraction of acetonitrile, x , are the independent variables, the third order polynomials shown in Table 4 are obtained. These equations permit assessment of pH_{PS} values in any acetonitrile-water mixture with an acetonitrile content up to 70% (w/w).

Although variation of the pH_{PS} values obtained in acetonitrile-water mixtures with x_{AN} is, for some cases, approximately linear in the mixtures studied (Fig. 1) these pH_{PS} are lower than those expected considering the high pH_{PS} values in the pure acetonitrile solvent (Table 3).

Figure 2 shows the pH_{PS} values as a function of the mole fraction of water x_w , the more polar constituent of the solvent mixtures, in the whole range of aqueous acetonitrile mixtures. pH_{PS} vs. x_w plots show deviations from a linear dependence on the composition variations of the mixture. A dotted line indicating linearity over the entire range (henceforth referred to as the ideal line) is also shown.

If the components of a binary solvent mixture participate randomly in the solvation of the solute, a linear relationship analogous to the Raoult law is expected

Table 2. Measured emf-values of cell B at various KCl concentrations in primary standard reference solutions for various acetonitrile-water mixtures at 298.15 K

Buffer solutions													
KH tartrate		KH citrate		Phosphate buffer I		Phosphate buffer II		Na tetraborate		Carbonate buffer		KH phthalate	
C_{KCl} (mM)	E (mV)	C_{KCl} (mM)	E (mV)	C_{KCl} (mM)	E (mV)	C_{KCl} (mM)	E (mV)	C_{KCl} (mM)	E (mV)	C_{KCl} (mM)	E (mV)	C_{KCl} (mM)	E (mV)
10 wt% Acetonitrile													
4.6	35.3	3.6	22.4	1.8	-184.5	3.7	-199.3	4.0	-306.5	5.4	-408.2	5.2	10.9
9.2	53.0	7.1	40.0	3.3	-169.7	7.4	-181.3	8.0	-289.2	10.7	-390.1	10.3	28.4
13.7	63.4	14.0	57.4	5.4	-156.8	14.7	-163.2	15.6	-271.9	20.8	-370.9	24.7	51.5
26.6	80.7	23.9	71.8	7.5	-148.4	28.8	-144.8	26.6	-258.3	34.9	-355.8	37.9	63.2
46.5	96.7	33.2	80.8	8.8	-144.0	39.1	-136.1	37.0	-249.5	47.8	-346.7	50.1	71.0
61.2	104.2	49.8	89.0	10.1	-140.3	52.3	-127.7	49.9	-241.5	67.4	-337.1	61.4	76.7
30 wt% Acetonitrile													
3.9	25.4	9.5	18.0	4.0	-172.6	3.9	-205.4	3.4	-361.1	4.1	-426.2	4.2	-16.4
7.8	43.5	12.5	25.2	7.9	-154.7	7.8	-187.2	6.7	-343.3	8.1	-408.3	8.2	1.3
15.4	62.1	21.3	39.3	19.3	-130.3	19.0	-163.1	16.4	-320.0	19.8	-384.7	16.2	19.3
29.7	80.7	29.6	48.2	30.0	-117.9	33.0	-147.6	25.5	-308.1	30.8	-372.8	27.5	33.8
36.4	86.7	32.2	50.6	40.1	-109.5	42.8	-140.1	36.8	-297.9	41.2	-364.8	38.2	42.9
49.2	95.5	42.4	58.1	52.8	-101.5	49.0	-136.1	44.8	-292.4	51.0	-358.7	48.4	49.5
40 wt% Acetonitrile													
3.2	20.3	5.2	23.2	3.5	-163.7	5.5	-198.7	6.4	-352.5	2.9	-432.5	4.0	-21.9
6.3	38.5	10.2	40.4	7.0	-145.8	10.8	-180.6	12.4	-335.4	5.7	-415.0	8.0	-4.0
12.4	57.0	17.3	54.2	17.1	-121.7	18.4	-166.1	20.9	-322.2	11.2	-397.2	15.7	13.9
21.1	71.9	26.2	65.4	26.5	-109.1	23.2	-159.6	31.3	-311.5	21.5	-379.3	26.6	28.4
29.3	81.5	30.4	69.4	35.5	-100.7	27.9	-154.4	35.9	-307.7	28.7	-371.0	37.0	37.6
39.6	90.3	38.4	75.9	41.2	-96.1	34.6	-148.2	40.4	-304.4	35.6	-364.8	50.0	46.1
50 wt% Acetonitrile													
15.0	45.4	2.9	-10.3	3.6	-183.6	2.4	-231.3	6.4	-355.0	4.2	-454.0	2.0	57.6
18.0	50.6	8.2	17.2	5.9	-170.7	7.0	-204.3	8.8	-346.5	8.1	-437.2	6.0	-29.2
23.7	58.7	13.3	29.7	10.3	-155.7	13.2	-187.3	15.4	-331.5	13.5	-420.9	9.8	-16.1
29.0	64.6	20.1	40.7	16.3	-142.9	20.5	-174.8	19.5	-325.1	18.3	-408.9	15.3	-4.2
34.0	69.4	28.2	50.2	21.6	-134.6	25.4	-168.2	26.8	-315.8	21.2	-403.2	20.5	4.2
40.8	75.2	33.7	55.2	28.0	-127.0	28.4	-164.9	30.2	-312.4	26.6	-394.6	25.4	10.1
70 wt Acetonitrile													
2.7	19.3	1.8	9.7									20.0	-33.7
5.2	38.7	2.6	17.6									4.8	-10.4
9.7	58.0	3.9	27.2									7.5	1.5
12.7	66.6	5.0	33.1									10.0	9.5
15.5	72.8	6.5	38.8									12.4	14.6
17.9	77.6	7.4	41.5									14.6	20.0

Table 3. Standard pH_{PS} values for primary standard reference solutions in various acetonitrile-water mixtures, together with their standard deviations (in parenthesis) at 298.15 K

Primary reference standard	% (w/w) acetonitrile-water						
	0 ^a	10	30	40	50	70	100
KH tartrate	3.557	3.802 (0.006)	4.325 (0.005)	4.570 (0.005)	4.852 (0.004)	5.723 (0.006)	17.79 (0.09)
KH_2 citrate	3.776	3.994 (0.007)	4.470 (0.008)	4.702 (0.006)	4.995 (0.003)	5.610 (0.005)	16.48 (0.09)
KH phthalate	4.008	4.318 (0.005)	5.015 (0.004)	5.346 (0.004)	5.644 (0.004)	6.428 (0.005)	16.82 (0.07)
Phosphate I	6.865	7.149 (0.007)	7.604 (0.003)	7.667 (0.004)	8.002 (0.005)	—	—
Phosphate II	7.413	7.697 (0.006)	8.151 (0.004)	8.436 (0.006)	8.646 (0.004)	—	—
Na tetraborate	9.180	9.600 (0.004)	10.437 (0.007)	10.807 (0.006)	11.204 (0.006)	—	—
Carbonate buffer	10.012	11.353 (0.046)	11.893 (0.007)	12.118 (0.006)	12.676 (0.007)	—	—

^a From reference [10]

[14, 15, 39]:

$$\text{pH}_{\text{PS}} = x_1 \text{pH}_{\text{PS}_1} + x_2 \text{pH}_{\text{PS}_2} \quad (5)$$

where pH_{PS} represents the primary standard pH -value in the acetonitrile-water mixture pH_{PS_1} , and pH_{PS_2} are the

primary standard pH -values in solvent 1 and 2, respectively, and x_1 and x_2 represent the mole fraction of the solvent 1 and 2 in the bulk solvent. From the plots of pH_{PS} -values in the mixtures vs. x_1 (1 being the more polar constituent of the solvent mixture), preferential solvation can be seen when a loss of ideal dependence is produced. If

Table 4. Relationships between pH-values and weight w and volume v percentages of acetonitrile and molar fraction of acetonitrile

KH tartrate	
$\text{pH}_{\text{PS}} = 3.547 + 3.02 \times 10^{-2}w - 2.92 \times 10^{-4}w^2 + 4.36 \times 10^{-6}w^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 3.546 + 2.49 \times 10^{-2}v - 2.60 \times 10^{-4}v^2 + 4.01 \times 10^{-6}v^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 3.552 + 5.995x - 9.158x^2 + 11.445x^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 9.18 - 8.97\pi^* + 3.35\alpha + 1.72\beta$	$r = 0.994$
KH citrate	
$\text{pH}_{\text{PS}} = 3.775 + 2.18 \times 10^{-2}w - 1.24 \times 10^{-5}w^2 + 7.13 \times 10^{-6}w^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 3.775 + 1.74 \times 10^{-2}v - 2.72 \times 10^{-7}v^2 + 1.15 \times 10^{-6}v^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 3.777 + 4.803x - 3.348x^2 + 2.011x^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 9.34 - 7.16\pi^* + 1.89\alpha + 0.97\beta$	$r = 0.999$
KH phthalate	
$\text{pH}_{\text{PS}} = 3.996 + 3.56 \times 10^{-2}w - 1.18 \times 10^{-4}w^2 + 1.49 \times 10^{-6}w^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 3.998 + 2.75 \times 10^{-2}v - 5.02 \times 10^{-5}v^2 + 1.38 \times 10^{-6}v^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 3.996 + 7.996x - 10.996x^2 + 9.604x^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 12.79 - 8.25\pi^* + 0.49\alpha + 0.14\beta$	$r = 0.999$
Phosphate (buffer I)	
$\text{pH}_{\text{PS}} = 6.853 + 4.03 \times 10^{-2}w - 9.05 \times 10^{-4}w^2 + 1.10 \times 10^{-5}w^3$	$r = 0.995$
$\text{pH}_{\text{PS}} = 6.885 + 3.16 \times 10^{-2}v - 5.84 \times 10^{-4}v^2 + 6.55 \times 10^{-6}v^3$	$r = 0.995$
$\text{pH}_{\text{PS}} = 6.850 + 8.729x - 38.057x^2 + 71.228x^3$	$r = 0.997$
$\text{pH}_{\text{PS}} = 11.18 - 4.92\pi^* + 0.62\alpha + 1.25\beta$	$r = 0.995$
Phosphate (buffer II)	
$\text{pH}_{\text{PS}} = 7.418 + 2.78 \times 10^{-2}w - 1.21 \times 10^{-4}w^2 + 1.19 \times 10^{-6}w^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 7.417 + 2.23 \times 10^{-2}v - 8.29 \times 10^{-5}v^2 + 1.23 \times 10^{-6}v^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 7.422 + 5.880x - 8.080x^2 + 6.588x^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 13.20 - 5.39\pi^* + 0.81\alpha + 0.58\beta$	$r = 0.998$
Na tetraborate	
$\text{pH}_{\text{PS}} = 9.178 + 4.34 \times 10^{-2}w - 6.36 \times 10^{-5}w^2 + 8.33 \times 10^{-8}w^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 9.178 + 3.35 \times 10^{-2}v - 1.51 \times 10^{-5}v^2 + 2.59 \times 10^{-7}v^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 9.176 + 9.942x - 15.152x^2 + 14.179x^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 19.79 - 8.27\pi^* + 0.99\alpha + 0.13\beta$	$r = 0.999$
Carbonate buffer	
$\text{pH}_{\text{PS}} = 10.020 + 0.186w - 6.23 \times 10^{-3}w^2 + 7.13 \times 10^{-5}w^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 10.014 + 0.145v - 4.43 \times 10^{-3}v^2 + 4.44 \times 10^{-5}v^3$	$r = 0.999$
$\text{pH}_{\text{PS}} = 10.055 + 34.364x - 197.679x^2 + 371.884x^3$	$r = 0.996$
$\text{pH}_{\text{PS}} = 8.91 - 11.26\pi^* + 6.95\alpha + 12.89\beta$	$r = 0.999$

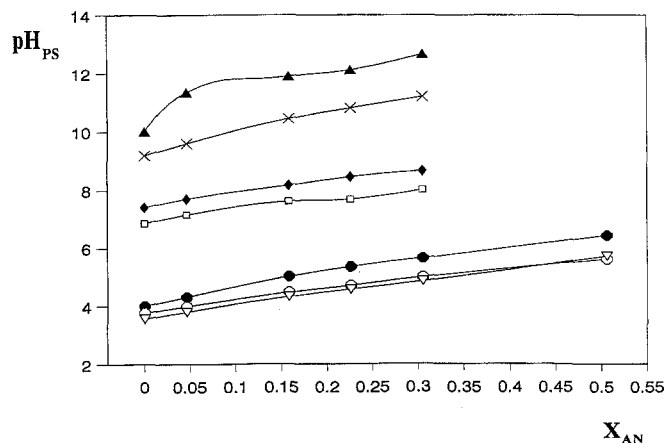


Fig. 1. Standard pH_{PS} values as a function of the compositions of the acetonitrile-water mixtures. Symbols: ∇ KH tartrate; \circ KH_2 citrate; \bullet KH phthalate; \square phosphate buffer I; \blacklozenge phosphate buffer II; \times Na tetraborate; \blacktriangle carbonate buffer

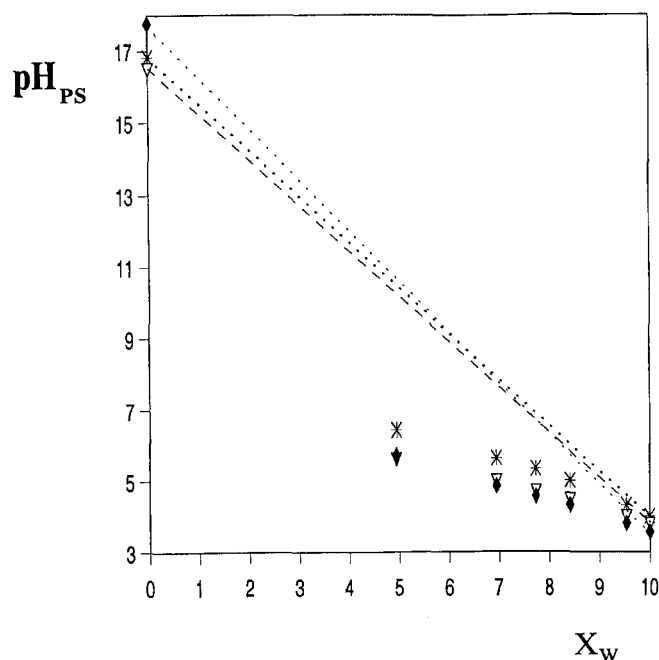


Fig. 2. Plot of pH_{PS} values vs. the mole fraction of water, x_w , in acetonitrile-water mixtures. \blacklozenge KH tartrate; ∇ KH_2 citrate; $*$ KH phthalate

a solute interacts with one of the solvents more strongly than with the other, the solute is preferentially solvated by the former. Preferential solvation in acetonitrile-water mixtures produces lower pH_{PS} values than those expected if the “preferred” solvent is water.

The QLQC theory of preferential solvation [19–21] has been applied to quantify the preferential solvation by water of the hydrogen ions in acetonitrile-water mixtures, δ_w . For this purpose, the standard molar Gibbs free energy of transfer for hydrogen ion from water into pure acetonitrile solvent, $\Delta G_i^\circ(\text{H}^+, \text{W} \rightarrow \text{AN})/\text{KJ mol}^{-1} = 46.4$ [40] and the excess of Gibbs free energy of mixing for acetonitrile-water equimolar mixtures, $G_{\text{WAN}}^E(x = 0.5) = 1.32 \text{ KJ mol}^{-1}$ [41], are required. The QLQC theory considers that each particle in the dilute solution of ions X in the mixed solvents S_1 and S_2 is surrounded by Z neighbours, the lattice parameter. Z has been assigned the value of 6 for different systems [20, 21], and this value was therefore selected for the system studied here.

The results from the QLQC method at 25 °C for the preferential solvation by water, δ_w , and for the local mole fraction of water, x_w^L around a hydrogen ion are plotted in Fig. 3 and shown in Table 5 as functions of the composition of the binary mixtures of water and acetonitrile. The preferential solvation of hydrogen ions by water is positive, i.e. water molecules show a greater tendency to be in the immediate vicinity of a given hydrogen ion than acetonitrile molecules. This preference is maximal at $x_w \approx 0.25$.

The preferential solvation obtained for hydrogen ions in aqueous acetonitrile can be related to the average number of water molecules in the vicinity of the hydrogen ion, n_w , given by the product $Z(\delta_w + x_w)$ and that of acetonitrile solvent $n_{\text{AN}} = Z(1 - \delta_w - x_w)$. These numbers for acetonitrile-water mixtures over the whole composition range are shown in Table 5.

The values of δ_w obtained are in accordance with the $\Delta G_i^\circ(X, \text{W} \rightarrow \text{S})$ sign [21]. A positive value of the standard Gibbs free energy of transfer $\Delta G_i^\circ(X, \text{W} \rightarrow \text{S})$, as is the case of $\Delta G_i^\circ(\text{H}^+, \text{W} \rightarrow \text{AN})$, means that the ion prefers water, and the preferential solvation δ_w is positive. There is however an important effect of the mutual interactions of the organic solvent with water in hydroorganic mixtures: if they repel each other, shown by a positive value of $G_{\text{SW}}^E(x = 0.5)$, as is the case of acetonitrile-water mixtures,

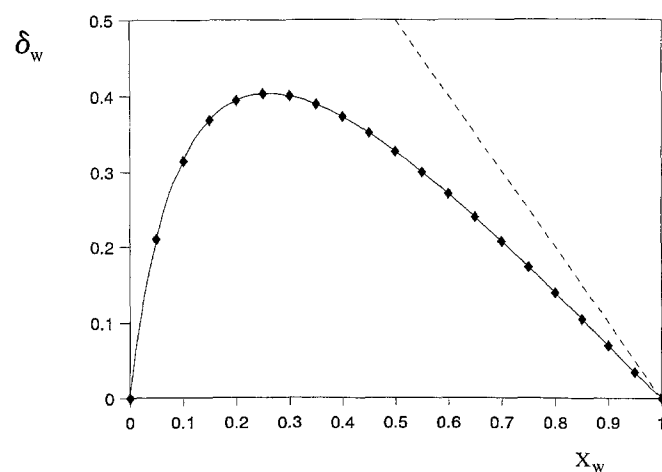


Fig. 3. Preferential solvation of hydrogen ions by water in acetonitrile-water mixtures, δ_w as a function of the solvent composition. The dashed straight line corresponds to total preference of water

Table 5. Results from the QLQC method at 25 °C

x_{AN}	x_w	δ_w	x_w^L	n_w	n_{AN}
0.05	0.95	0.03	0.98	5.9	0.1
0.10	0.90	0.07	0.97	5.8	0.2
0.15	0.85	0.10	0.95	5.7	0.3
0.20	0.80	0.14	0.94	5.6	0.4
0.25	0.75	0.17	0.92	5.5	0.5
0.30	0.70	0.21	0.91	5.4	0.6
0.35	0.65	0.24	0.89	5.3	0.7
0.40	0.60	0.27	0.87	5.2	0.8
0.45	0.55	0.30	0.85	5.1	0.9
0.50	0.50	0.33	0.83	5.0	1.0
0.55	0.45	0.35	0.80	4.8	1.2
0.60	0.40	0.37	0.77	4.6	1.4
0.65	0.35	0.39	0.74	4.4	1.6
0.70	0.30	0.40	0.70	4.2	1.8
0.75	0.25	0.40	0.65	3.9	2.1
0.80	0.20	0.39	0.59	3.6	2.4
0.85	0.15	0.37	0.52	3.1	2.9
0.90	0.10	0.31	0.41	2.5	3.5
0.95	0.05	0.21	0.26	1.6	4.4

the tendency produced by $\Delta G_i^\circ(X, \text{W} \rightarrow \text{S})$ is greatly enhanced. The results, in terms of preferential solvation by water δ_w (Fig. 3, Table 5) are similar to those also obtained for chloride ions in aqueous acetonitrile [21] with a similar $\Delta G_i^\circ(\text{Cl}^-, \text{W} \rightarrow \text{AN}) \text{ KJ mol}^{-1} = 42.1$ [40]. Therefore, as the preferential solvation of hydrogen ions by water is positive, the standard pH_{PS} values in these mixtures are more similar to the standard pH_{PS} values in water than those in acetonitrile (Fig. 2). This is different for compositions close to the pure acetonitrile solvent [39, 42] where $x_w < 0.25$ and the preferential solvation by water decreases quickly (Fig. 3).

The pH_{PS} values obtained could be explained in terms of the structural features of the acetonitrile-water mixtures. The structure of mixtures of water and acetonitrile was explored by the use of QLQC and the inverse Kirkwood-Buff integral (IKBI) methods [22, 43]. The authors concluded that these methods point toward strong microheterogeneity in the middle range of compositions in mixtures of water and acetonitrile, i.e. preference for neighbours of the same kind, which extends over several concentric shells around a given molecule. Thus, there is a preference of a given water molecule for water molecules rather than acetonitrile molecules. This preference is maximal at $x_{\text{AN}} \approx 0.75$. The same applies to the preference of acetonitrile molecules for being in the vicinity of a given acetonitrile molecule. Thus, the plot of pH_{PS} values vs x_w (Fig. 2) can be explained taking into account that in acetonitrile-water mixtures there are three regions [22, 27, 29, 44]. On the water-rich side there is a region in which the water structure remains more or less intact and the acetonitrile molecules gradually occupy the cavities between water molecules without disruption of the water structure [45]. The limit of x_{AN} beyond which the acetonitrile can no longer be accommodated within the cavities of the structure of water is about 0.15 [22]. In this water-rich region the slopes of pH_{PS} vs. x_w plots are greater than their slopes in the region where acetonitrile-water mixtures show microheterogeneity (Fig. 2). This is

in accordance with the low value of δ_w in $x_{AN} < 0.15$ acetonitrile-water mixtures (Fig. 3).

In the range $0.15 \leq x_{AN} \leq 0.75$ there are clusters of molecules of the same kind surrounded by regions where molecules of both kinds are near each other. In this middle range of compositions, preferential solvation of hydrogen ions by water is high (Fig. 3). This could explain the low slope of the linear variations of pH_{PS} vs. x_w plots (Fig. 2). At $x_{AN} \geq 0.75$ the number of water clusters is low and water-acetonitrile interactions, that could be discounted in the middle range, now become important. This may be considered as a region in which δ_w decreases (Fig. 3), and then a concave variation of pH_{PS} vs. x_w may be expected with one inflection point at $x_w = 0.25$, where preferential solvation by water of hydrogen ions is maximal (Fig. 3). The boundaries of the regions are, of course, not sharp [22].

On the other hand, it is not evident that solvatochromic parameters can be used for generalized solutes in binary solvent mixtures. Studies have already been reported [22, 46] that provide significant evidence that the solvatochromic parameters seem to have general validity although this problem is not solved unequivocally. It is, therefore, of interest to explore in acetonitrile-water mixtures the use of solvatochromic solvent properties π^* , α and β , which are so successful in linear solvation energy relationships (LSER) involving non-aqueous pure solvents. For the description of LSERs the Kamlet-Taft [47] expression, which explains any solute property varying with solvent composition as a linear combination of solvatochromic parameters of the solvent, was found to be successful:

$$XYZ = (XYZ)_0 + a\alpha + b\beta + s\pi^* \quad (6)$$

where α , β and π^* are the microscopic parameters previously described, XYZ is the solute property, XYZ_0 the value of this property for the same solute in a hypothetical solvent for which $\alpha = \beta = \pi^* = 0$ and a , b and s are the susceptibilities of the solute property studied to changes in α , β and π^* , respectively. This equation can include additional terms or some of its terms can become equal to zero, depending on the property of the solute to be described [47]. Values of the Kamlet-Taft solvatochromic parameters π^* [22, 48], α [22, 49] and β [16, 22] for acetonitrile-water mixtures over the entire range of composition are known [42].

In the present paper, severe attempts were made to find the best form of the Kamlet-Taft equation to describe the variation of standard pH_{PS} values in acetonitrile-water mixtures. Multiple regression analysis was applied to our pH_{PS} data. All possible combinations of solvatochromic parameters were checked. The best fit was obtained when the three solvatochromic parameters α , β and π^* were used, yielding the general equations shown in Table 4. The small coefficients in the α and β terms compared with the π^* terms confirm the main dependence of the standard pH_{PS} values on the microscopic polarity of the solvent (expressed by π^*) for the whole range of compositions studied, up to 70% (w/w) of acetonitrile, in acetonitrile-water mixtures. From a practical point of view, the equations given in Table 4 enable us to assign the standard pH_{PS} values of the buffer reference solutions

studied in any of the binary solvent acetonitrile-water mixture, and thus permit the standardization of potentiometric sensors in these mixtures.

It must be emphasized that each pH_{PS} value is valid only for the pH scale relevant to the specific mixed solvent considered [4, 28]. Values of pH_{PS} pertaining to different solvents would become physically comparable in an "intersolvent" pH-scale with ultimate reference to the familiar pH-scale in water only if the primary medium effect upon H^+ is considered:

$$\text{pH} = \text{pH}_{\text{PS}} + \log \gamma_{\text{w-s}}^{\text{t}}(\text{H}^+) \quad (7)$$

$\gamma_{\text{w-s}}^{\text{t}}(\text{H}^+)$, the primary medium effect, is a measure of the Gibbs free energy of transfer of the H^+ ion from water to the solvent mixture, and as such is another extrathermodynamic quantity.

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