

Short Communication

pH measurements in acetonitrile–water mixtures by use of a glass electrode*

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Introduction

Methods for optimizing the resolution of chromatographic separation usually focus on the optimization of the mobile phase composition and pH [1, 2]. However, procedures for the optimization of solvent composition are currently much more advanced than procedures for pH optimization [3], although in a number of situations the concentration of organic modifier has a much less dramatic effect than pH on the efficiency and peak symmetry [4]. The mobile phase pH is potentially a very useful parameter for achieving and optimizing ionogenic solute resolution in reversed-phase LC.

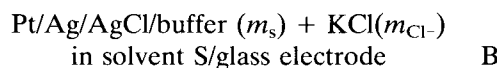
For successful systematic optimization of the mobile phase pH, accurate pH measurements in the more widely used binary aqueous–organic solvent mixtures are needed. The pH in aqueous–organic mixtures such as acetonitrile–water is in principle not the same as that in pure water [5, 6]. The measurement of pH in mixed solvents is based upon operational definitions of pH [7] in which the pH is estimated by

$$pH_x = pH_{PS} + (E_{PS} - E_x)/g, \quad (1)$$

where the pH of solution X, pH_x , is related to the pH of a primary standard reference sol-

ution, pH_{PS} , and the electromotive force of the cell A, this being $g = (\ln 10) RT/F$.

As shown by equation (1), for pH measurements in water + organic solvent mixtures, reliable reference value standards, pH_{PS} , in these media are required. The latter, as prescribed by IUPAC specific standardization rules [8, 9], are obtained by measuring the e.m.f. [8, 9] of a reversible cell of the type:



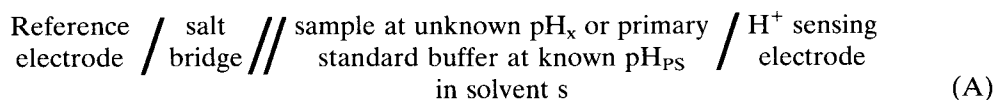
at 298.15 K, at fixed molality m_{PS} for the primary standard but at various molalities m_{Cl^-} of KCl added to the buffer solution in the aqueous–organic solvent mixtures.

The Nernstein expression for the e.m.f. of the cell B, E_B , can be calculated conveniently as follows, using concentrations:

$$(E_B - E^0)/g - pc_{Cl^-} = p(a_{H^+}y_{Cl^-}) = pH + py_{Cl^-}, \quad (2)$$

where E^0 is the standard e.m.f. of the cell in the appropriate solvent mixture.

Equation (2) shows that the quantity $p(a_{H^+}y_{Cl^-})$ which differs from pH just by py_{Cl^-} , the molar activity coefficient, is determinable in exact thermodynamic terms but an extra-



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thermodynamic assumption, in terms of a Debye–Hückel equation of the type

$$py_{\text{Cl}^-} = AI^{1/2}/(1 + a_0BI^{1/2}) \quad (3)$$

is necessary to obtain the two extrathermodynamic quantities pH and py_{Cl^-} . A and B are the Debye–Hückel constants, a_0 is the ion size parameter in the solvent mixture considered fixed by the Bates–Guggenheim rule [9, 10], and I is the ionic strength obtained by an iterative calculation through the ionization constants relevant to the buffer substance [11, 12]. The pH values obtained from equation (2) are then plotted against c_{Cl^-} and the intercept at $c_{\text{Cl}^-} = 0$ is taken as the standard value pH_{PS} .

The aim of the present work was the assessment of pH_{PS} values for three primary standard buffer solutions (KH tartrate, KH phthalate and phosphate buffer) in acetonitrile–water mixtures containing 10, 30, 40, 50 and 70% (w/w) acetonitrile. The above determinations of pH_{PS} values require the relevant E^0 values of cell B and the ionization constants, $\text{p}K$, of all three standards studied covering those acetonitrile–water mixtures containing up to 70% (w/w) acetonitrile at 298.15 K which were determined previously [10, 12]. Relationships between the pH_{PS} values and different characteristics of the solvent mixtures were examined and the linear solvation energy relationships method (LSER) [3, 13, 14] applied in order to obtain the pH_{PS} values in each of the unlimited number of possible binary solvent acetonitrile–water mixtures.

Experimental

Apparatus

The e.m.f. values of the potentiometric cell B 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 [15]. The cell was thermostatted externally at $25 \pm 0.1^\circ\text{C}$. The potentiometric assembly was automatically controlled with a Stronger AT microcomputer.

Reagents

Analytical reagent grade chemicals were used unless otherwise indicated. All the solutions were prepared by mixing doubly distilled freshly boiled water and acetonitrile

(Merck, chromatography grade). Before use, the primary standards (Merck, A.R.) were dried at 110°C .

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 measured by the IUPAC procedure [9]. This involved e.m.f. measurements of cell B containing the primary buffer solutions with added potassium chloride. The concentrations of the primary standards used in this work were those recommended as International pH Standards [16].

Results and Discussion

The e.m.f., E , of cell B was measured at different molalities c_{Cl^-} of KCl added to the constant concentration of each primary buffer recommended as International pH Standards [16], in 10, 30, 40, 50 and 70% (w/w) acetonitrile–water solvent composition. For each primary standard various series of measurements were made, for a total of 336 independent measurements over the solvent interval explored. To simplify the tabulation, E values for only one series of different KCl concentrations in each primary standard reference solution are quoted in Table 1.

To obtain pH values for the mixed electrolyte in cell B (equation 2) values of the standard e.m.f. of the cell E^0 , are essential and have been determined previously [10]. Also, it is indispensable to calculate py_{Cl^-} (equation 3). Calculation of py_{Cl^-} requires knowledge of the ionic strength, I , of the primary buffer + KCl mixed electrolyte solution, but I is, in turn, a function of the H^+ concentration, c_{H^+} , and of the ionization constants, $\text{p}K$, corresponding to the equilibria involved in the primary standard reference solutions in acetonitrile–water mixtures. The required $\text{p}K$ values ($\text{p}K_1$ and $\text{p}K_2$ of tartaric and phthalic acids and $\text{p}K_2$ of phosphoric acid) were determined previously [12], and calculation of py_{Cl^-} values proceeded by successive iterations.

Inserting py_{Cl^-} in equation (2) gave one distinct pH value for each concentration c_{Cl^-} examined. The standard value, pH_{PS} , for primary buffer alone at the molality recommended for International pH Standards was obtained as the intercept at $c_{\text{Cl}^-} = 0$ from the pH vs c_{Cl^-} linear regression at each mole

Table 1

Measured e.m.f. values of cell B, molar activity coefficients of monoprotated species and pH values at various KCl concentrations in various acetonitrile-water mixtures at 298.15 K

KH tartrate			Buffer solutions KH phthalate			Phosphate buffer		
C_{Cl^-}	E	pH	C_{Cl^-}	E	pH	C_{Cl^-}	E	pH
10 wt% Acetonitrile								
7.8	53.5	3.782	7.9	21.8	4.306	6.8	-151.1	7.140
11.6	63.9	3.775	15.5	39.3	4.298	7.4	-148.5	7.127
15.4	71.4	3.766	22.9	49.4	4.292	8.1	-146.1	7.134
22.6	81.6	3.756	29.9	56.5	4.285	8.8	-144.0	7.132
29.6	89.2	3.740	33.4	59.4	4.282	9.4	-142.0	7.129
36.3	94.8	3.731	40.0	64.2	4.277	10.1	-140.1	7.126
30 wt% Acetonitrile								
3.9	27.9	4.316	7.2	-2.5	5.011	7.9	-154.0	7.588
7.8	46.1	4.301	17.5	21.3	4.987	15.6	-136.1	7.576
15.4	64.4	4.274	24.0	30.3	4.974	26.5	-121.6	7.557
22.7	75.1	4.253	30.3	36.4	4.963	33.4	-115.1	7.546
29.7	82.7	4.235	36.3	41.5	4.953	40.1	-109.9	7.535
36.4	88.5	4.220	42.2	45.7	4.943	46.6	-105.6	7.525
40 wt% Acetonitrile								
9.4	49.2	4.544	4.0	-21.9	5.340	7.0	-146.1	7.653
15.3	62.7	4.520	8.0	-4.0	5.331	13.8	-127.8	7.633
21.1	71.6	4.499	15.7	13.9	5.315	20.3	-117.0	7.616
23.9	75.1	4.491	23.0	24.4	5.300	26.5	-109.3	7.600
26.6	78.2	4.482	33.6	34.8	5.281	29.6	-106.1	7.592
31.9	83.4	4.468	40.3	40.0	5.269	32.6	-103.3	7.585
50 wt% Acetonitrile								
11.9	39.4	4.812	4.1	-39.7	5.636	3.6	-183.8	7.993
18.0	51.4	4.778	9.8	-16.1	5.618	8.2	-162.5	7.982
23.7	59.6	4.750	15.3	-4.2	5.604	14.3	-146.8	7.959
29.0	65.7	4.728	18.8	1.8	5.588	19.9	-137.3	7.938
34.0	70.5	4.708	22.2	6.3	5.581	24.9	-130.7	7.922
38.6	74.4	4.693	25.4	10.1	5.573	28.0	-127.3	7.913
70 wt% Acetonitrile								
4.9	39.0	5.680	6.0	-29.1	5.628			
7.9	53.2	5.629	9.9	-16.1	5.617			
10.5	62.4	5.591	13.5	-7.5	5.607			
13.0	69.0	5.563	17.1	-1.2	5.598			
15.2	74.2	5.539	20.5	4.2	5.548			
16.3	76.4	5.529	25.4	10.2	5.573			

Table 2

pH_{PS} values for Primary Standard Reference Solutions and values of dissociation constants of the equilibria involved in various acetonitrile-water mixtures at 298.15 K

Primary standard		% (w/w) Acetonitrile					
		0	10	30	40	50	70
KH tartrate	pH _{PS}	3.557	3.802	4.325	4.570	4.852	5.723
	pK ₁	3.03	3.27	3.73	4.00	4.29	5.17
	pK ₂	4.36	4.57	5.02	5.30	5.57	6.52
KH phthalate	pH _{PS}	4.008	4.318	5.013	5.346	5.644	6.429
	pK ₁	2.95	3.15	3.60	3.82	4.08	4.77
	pK ₂	5.41	5.77	6.86	7.31	7.75	9.06
Phosphate	pH _{PS}	6.865	7.149	7.604	7.667	8.002	
Buffer	pK ₂	7.20	7.46	8.02	8.24	8.53	9.42

fraction x of acetonitrile studied. Typical regression lines are shown in Fig. 1 for the KH tartrate in the acetonitrile-water solvent mixtures studied.

Table 2 shows the pH_{PS} values determined for the KH tartrate, KH phthalate the phosphate buffer primary standard reference buffer solutions in 10, 30, 40, 50 and 70% (w/w)

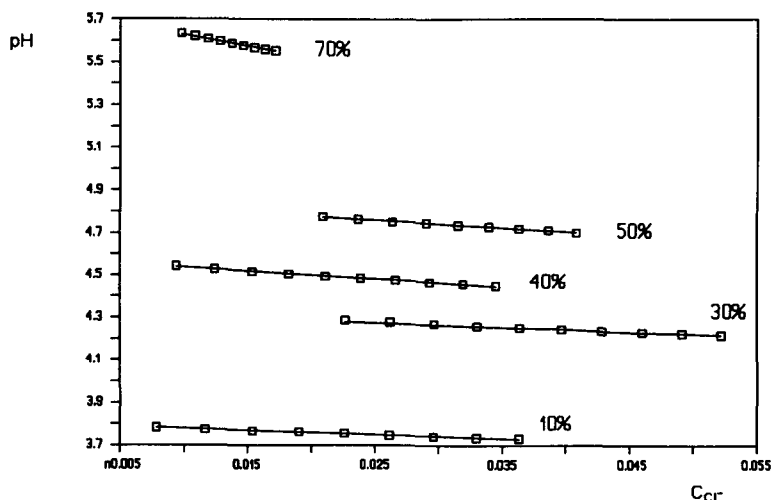


Figure 1

Plot of the pH vs the chloride concentration, c_{Cl^-} , for the Primary Standard Reference Standard, KH tartrate in various acetonitrile–water mixtures.

Table 3

Relationships between pH_{PS} values and weight w , volume v percentages and molar fraction of acetonitrile in admixtures with water and linear solvation energy relationships for pH_{PS} values

KH tartrate

$$pH = 3.547 + 3.02 \times 10^{-2} w - 2.92 \times 10^{-4} w^2 + 4.36 \times 10^{-6} w^3 \quad r = 0.999$$

$$pH = 3.546 + 2.49 \times 10^{-2} v - 2.60 \times 10^{-4} v^2 + 4.01 \times 10^{-6} v^3 \quad r = 0.999$$

$$pH = 3.552 + 5.995 x - 9.158 x^2 + 11.445 x^3 \quad r = 0.999$$

$$pH = 12.186 - 9.576 \pi^* + 2.959 \alpha - 2.634 \beta \quad r = 0.991$$

KH phthalate

$$pH = 3.996 + 3.56 \times 10^{-2} w - 1.18 \times 10^{-4} w^2 + 1.49 \times 10^{-6} w^3 \quad r = 0.999$$

$$pH = 3.998 + 2.75 \times 10^{-2} v - 5.02 \times 10^{-5} v^2 + 1.38 \times 10^{-6} v^3 \quad r = 0.999$$

$$pH = 3.996 + 7.996 x - 10.966 x^2 + 9.604 x^3 \quad r = 0.999$$

$$pH = 13.032 - 8.499 \pi^* + 1.336 \alpha - 1.716 \beta \quad r = 0.996$$

Phosphate buffer

$$pH = 6.853 + 4.03 \times 10^{-2} w - 9.05 \times 10^{-4} w^2 + 1.10 \times 10^{-5} w^3 \quad r = 0.995$$

$$pH = 6.855 + 3.16 \times 10^{-2} v - 5.84 \times 10^{-4} v^2 + 6.55 \times 10^{-6} v^3 \quad r = 0.995$$

$$pH = 6.850 + 8.729 x - 38.057 x^2 + 71.228 x^3 \quad r = 0.997$$

$$pH = 12.008 - 3.883 \pi^* - 0.105 \alpha - 0.996 \beta \quad r = 0.993$$

acetonitrile–water mixtures together with standard pH_{PS} values reported in water [17].

Determination of pH_{PS} values must be carried out at each distinct composition of the solvent but considering the unlimited number of possible binary solvent acetonitrile–water mixtures, some procedure for predicting pH_{PS} values, including pure water as an extreme case, is desirable. To this end the different sets of results for the various solvent mixtures investigated were analysed by a multilinear regression procedure. The commonly used concentration by volume % (v/v), v , the molar fraction of acetonitrile, x , or % (w/w), w , are

the independent variables and third-order polynomials shown in Table 3 were obtained.

To provide an independent interpretation of pH_{PS} results, the linear solvation energy relationships (LSER) method, based on the Kamlet–Taft multiparameter scales [13] was utilized. The solvatochromic LSER approach of Kamlet and Taft seeks to relate as a pH_{PS} value or a dissociation constant value, XYZ , with three types of terms, based on the differential evaluation of solvent dipolarity/polarizability (π^*) solvent hydrogen bond donating acidity (α) and solvent hydrogen bond accepting basicity (β), as shown below.

$$XYZ = XYZ_0 + a\alpha + b\beta + s\pi^*. \quad (4)$$

The terms a , b and s represent the susceptibilities of XYZ to changing solvent solvatochromic properties [18]. Values of the Kamlet–Taft solvatochromic parameters π^* [14], α [19] and β [20] for acetonitrile–water mixtures are known. As a result of application of the LSER method to pH_{PS} values determined in this work, the relationships shown in Table 3 were obtained. These equations allow knowledge of the pH_{PS} value of a primary standard buffer in any acetonitrile–water mixture.

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