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REFERENCE VALUE STANDARDS AND PRIMARY STANDARDS FOR pH MEASUREMENTS IN D_2O AND AQUEOUS–ORGANIC SOLVENT MIXTURES: NEW ACCESSIONS AND ASSESSMENTS

(Technical Report)

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Reference value standards and primary standards for pH measurements in D_2O and aqueous–organic solvent mixtures: New accessions and assessments (Technical Report)

Abstract: Recommended Reference Value Standards based on the potassium hydrogenphthalate buffer at various temperatures are reported for pH measurements in various binary solvent mixtures of water with eight organic solvents: methanol, ethanol, 2-propanol, 1,2-ethanediol, 2-methoxyethanol ("methylcellosolve"), acetonitrile, 1,4-dioxane, and dimethyl sulfoxide, together with Reference Value Standards based on the potassium deuterium phthalate buffer for pD measurements in D_2O. In addition are reported Primary Standards for pH based on numerous buffers in various binary solvent mixtures of water with methanol, ethanol, and dimethyl sulfoxide, together with Primary Standards for pD in D_2O based on the citrate, phosphate and carbonate buffers.

INTRODUCTION

Recently, new significant data on pH standards in aqueous organic solvent mixtures have been published (refs. 1-4). These new data are based on measurements of reversible electromotive force (e.m.f.) of the cells:

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{KHPh + KCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \mid \mathrm{Pt} \qquad (1)$$

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{Tris + TrisHCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \mid \mathrm{Pt} \qquad (2)$$

Data for 0.05 $\mathrm{mol{\cdot}kg^{-1}}$ potassium hydrogen phthalate (KHPh) buffer solution, *i.e.*, the Reference Value Standard for pH ($\mathrm{pH_{RVS}}$ according to IUPAC terminology (refs. 5,6)), in 1,2-ethanediol/water mixtures of mass fraction w(ethanediol) = 10%, 30%, 50%, and 70% (ref. 1) are the only available example of pH standards in diol/water mixtures. Data for equimolal Tris+TrisHCl buffer (Tris = tris(hydroxymethyl) methylamine) in 50% mass fraction ethanol/water mixtures (ref. 2) constitute an important primary standard ($\mathrm{pH_{PS}}$) for biomedical applications, and they supplement earlier $\mathrm{pH_{PS}}$ data for Tris+TrisHCl in 50% mass fraction methanol/water mixtures (ref. 7).

The e.m.f., E_{pH}, of both cells (1) and (2) is expressed as:

$$(E_{\mathrm{pH}} - E^\circ)/k = \mathrm{pH} + \mathrm{p}(m_{\mathrm{Cl}}\gamma_{\mathrm{Cl}}) \qquad (3)$$

where $k = (\ln 10)RT/F$, E° is the standard e.m.f. of the cell, p = −lg, and m_{Cl} and γ_{Cl} are the molality and the single-ion activity coefficient of the chloride ion, respectively. The E° value required by eq. (3) is determined from measurements of reversible e.m.f. of the cell:

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{HCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \mid \mathrm{Pt} \qquad (4)$$

in the appropriate solvent mixtures. The relevant e.m.f. expression is:

$$E_4 = E^\circ + 2k\,\mathrm{p}(m\gamma_\pm)_{\mathrm{HCl}} \qquad (5)$$

The recommended schemes for obtaining E° from E_4 and pH from E_{pH} are described elsewhere (refs. 5,6,8-10).

The E° values determined by different groups show significant inconsistencies both for water and aqueous organic solvent mixtures, whereas the values of the mean molal activity coefficients of HCl determined

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from ($E_4 - E°$) are in good agreement. This was why, some forty years ago, a group of leading electrochemists (ref. 11) proposed to adopt a "reverse standardization" of cell (4) based on internationally accepted values of $\gamma_\pm$. This approach recognizes the underlying problem, that $E°$ depends on the design and preparation methods of the hydrogen electrode and the silver/silver-chloride electrode used in cell (4) (as well as (1) and (2)). Indeed, the $p\gamma_\pm$, $p\gamma_{Cl}$ and pH values are characteristic of the relevant solutions, and not of the electrode type. Therefore, for the optimum condition of pH consistency, the same electrode pair, prepared by the same group of workers, should be used both in cell (4) for $E°$, and in cells (1) or (2) for pH. Dissymmetry and systematic performance deviations arising from electrode preparation method or different cell design are thus eliminated. This ideal condition has been seldom fulfilled. As a consequence, there are problems of re-assessment when new data sets become available for consolidation with earlier ones.

AGGREGATION AND RE-ASSESSMENT OF pH STANDARDS

All the available E_{pH} values for the whole range of compositions of aqueous mixtures with each organic solvent studied hitherto were usually measured by one group, whereas the E_4 values were often measured by a number of groups, each covering a narrow range of solvent mixture compositions. This made it necessary to aggregate the sparse E_4 data into a single set and to interpolate the "best" $E°$ value for the required solvent composition by appropriate regression analysis. Whilst this "best" value is an acceptable approach to the "true" $E°$ value, in terms of statistical treatment of errors, it may not exactly coincide with the required $E°$ value consistent with the E_{pH} measurements leading to pH through eq. (3). This situation is not beneficial for the accuracy of pH_{RVS} assignment. In particular, this is true for the ethanol/water mixtures, where E_{pH}'s were measured by one group (ref. 12) at four ethanol mass fractions (10, 20, 40, and 70%) whereas the same group measured the E_4 values at 70% ethanol only (ref. 13), using data for other compositions obtained by different groups (refs. 15-21). Besides providing, first of all, the pH_{PS} values for the Tris+TrisHCl buffer in 50% ethanol/water mixtures, the recent work by White and Warner (ref. 2) has also bearing on the pH_{RVS} values for the KHPh buffer in providing a sound set of E_4 values at temperatures from −10 to +25 °C. The latest $E°$ redetermination concerns 20 and 40% mass fractions of ethanol in water as well as 30 and 50 % mass fractions of 1,2-ethanediol in water mixtures (ref. 14).

By processing the resulting combined set of E_4 data one obtains revised $E°$ values which show significant deviations from the previously reported smoothed $E°$ values. This inevitably affects the pH_{RVS} values *directly*, because they are calculated from eq. (3), as well as *indirectly*: the latter effect arises from the ionization pK values of the o-phthalic acid, H_2Ph, which are required as ancillary data for processing the E_{pH} values, and are based on measurements of reversible e.m.f. of the cell:

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{H_2Ph{+}KHPh{+}KCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \mid \mathrm{Pt} \qquad (6)$$

When analysing the e.m.f. of cell (6) in terms of the Nernst equation, $E°$ value is ahgain needed. However, this indirect influence is of minor importance.

For **ethanol/water** mixtures, using the recommended multilinear regression procedure (refs. 5,6,22,23) the optimized $E°$ values can be expressed as a function of temperature and solvent composition by:

$$\begin{aligned}(E°/T)\,/\,(\mathrm{V{\cdot}K^{-1}}) = {} & 0.00074547 - 0.00060555x + 0.001114x^2 - 0.0016467x^3 - 0.0013902u_1 \\ & - 0.005294u_1x^{1/2} + 0.06087u_1x - 0.2072u_1x^{3/2} + 0.2409u_1x^2 - 0.1131u_1x^3 \\ & - 0.001673u_2 - 0.03700u_2x + 0.1953u_2x^2 - 0.2572u_2x^3 \end{aligned} \qquad (7)$$

where $u_1 = z/(1+z)$, $u_2 = \ln(1+z) - u_1$, $z = (T-\theta)/\theta$, $\theta = 298.15$ K, and x is the mole fraction of the organic component of the solvent mixture.

The $E°$ values for the ($E_{pH} - E°$)/k term in eq. (3) were obtained from eq. (7) for all the ethanol/water mixtures studied, even if $E°$ assignments for the 70 percent mixture could be taken from the work by Longhi *et al.* (refs. 12,13). This was possible because the same electrode pair was used for measuring both E_4 (ref. 13) and E_{pH} (ref. 12). However, in this case the difference in $E°$ values is negligible (0.02 mV, or 0.0003 in pH). All E_{pH} values which meet the IUPAC criteria (refs.5,6) for the KHPh buffer in ethanol/water mixtures have been analysed according to the IUPAC-endorsed multilinear regression procedure (refs. 5,6), yielding equation (8) for pH_{RVS}:

$$\begin{aligned}\mathrm{pH}_{\mathrm{RVS}} = {} & 3.99865 - 0.46452x^{1/2} + 9.5545x - 8.4053x^{3/2} \\ & + 0.33846u_1 + 5.5791u_1x + 23.938u_1x^2 + 9.699u_2 + 13.71u_2x \end{aligned} \tag{8}$$

Equation (8) allows interpolation of revised $\mathrm{pH}_{\mathrm{RVS}}$ values for the required solvent compositions and temperatures within the ranges investigated (see Table 1). The same terms seem likely applicable to the re-

TABLE 1. Values of pH-metric reference value standards (**$\mathrm{pH}_{\mathrm{RVS}}$**) for the **0.05 mol·kg^{-1} Potassium Hydrogen Phthalate (KHPh) buffer** in **aqueous-organic solvent mixtures** at various percentages of the nonaqueous component (with corresponding mole fractions x), at various temperatures t/°C, with overall estimated standard errors δ.

		Mass fraction of nonaqueous solvent in admixture with water										
		5%	10%	15%	20%	30%	40%	50%	64%	70%	80%	84.2%
	x t/°C		**0.0588**		**0.1232**			**0.3599**	**0.4999**			**0.7498**
METHANOL	10		4.254		4.490			5.151	5.488			6.254
	25		4.243		4.468			5.125	5.472			6.232
Ref. 5	40		4.257		4.472			5.127	5.482			6.237
	δ		± 0.003		± 0.003			± 0.003	± 0.003			± 0.003
	x t/°C		**0.0416**		**0.0891**		**0.2068**			**0.4771**		
	-5		4.278		4.567		5.113			5.530		
ETHANOL	0		4.261		4.544		5.078			5.505		
	10		4.238		4.510		5.022			5.474		
Refs.	25		4.230		4.488		4.973			5.466		
12,14,25	40		4.248		4.494		4.959			5.499		
	δ		± 0.002		± 0.002		± 0.002			± 0.002		
	x t/°C		**0.0322**			**0.1139**		**0.2306**		**0.4116**		
2-PROPANOL	15		4.259			4.881		5.247		5.510		
	25		4.249			4.850		5.210		5.522		
Ref. 26	35		4.253			4.834		5.189		5.548		
	45		4.270			4.833		5.182		5.584		
	δ		± 0.002			± 0.002		± 0.003		± 0.004		
	x t/°C		**0.0312**			**0.1106**		**0.2250**		**0.4038**		
	-10		-			4.441		4.845		-		
1,2-ETHANE-	-5		-			4.432		4.827		-		
DIOL	5		4.122			4.419		4.802		-		
	15		4.121			4.416		4.790		5.254		
	25		4.127			4.419		4.790		5.238		
Refs. 3,14	35		4.139			4.421		4.799		5.241		
	45		4.156			4.450		4.817		5.261		
	δ		± 0.002			± 0.002		± 0.002		± 0.002		
	x t/°C				**0.0559**			**0.1914**			**0.4864**	
	-10				-			5.534			6.878	
	-5				4.546			-			-	
2-METHOXY-	0				4.526			5.470			6.819	
ETHANOL	10				4.515			5.422			6.757	
	25				4.505			5.380			6.715	
	35				4.508			-			6.716	
Ref. 4	37				-			5.363			-	
	45				4.514			-			-	
	δ				± 0.003			± 0.002			± 0.003	
ACETO-	x t/°C	**0.0226**		**0.0719**		**0.1583**		**0.3050**		**0.5059**		
NITRILE	15	4.163		4.533		5.001		5.456		6.159		
	25	4.166		4.533		5.000		5.461		6.194		
Refs. 27,28	35	4.178		4.542		5.008		5.475		6.236		
	δ	± 0.005		± 0.005		± 0.005		± 0.005		± 0.005		
	x t/°C		**0.0222**			**0.0806**		**0.1697**				
1,4-DIOXANE	15		*4.330*			*5.034*		*5.779*				
	25		4.329			5.015		5.782				
	35		4.337			5.007		5.783				
Ref. 29	45		4.355			5.008		5.783				
	δ		± 0.002			± 0.002		± 0.002				
DIMETHYL	x t/°C				**0.0545**	**0.0899**						
SULFOXIDE	-12				-	4.870						
	+25				4.471	4.761						
Ref. 30	δ				± 0.002	± 0.002						

TABLE 2 - Values of primary standards (pH_{PS}) for different solvents or aqueous organic solvent mixtures at various temperatures, taken or recalculated from the given references. Values not fully complying with the IUPAC criteria (ref. 5) are quoted in parentheses ( ); values not satisfying F-tests are quoted in brackets [ ]. All % values for solvents in admixture with water are by mass fraction. The standard values in deuterium oxide are in terms of pD_{PS}.

BUFFERS		*ACETATE* ***a***	*SUCCINATE* ***b***	*PHOSPHATE* ***c***	*TRIS* + *TRIS*HCl ***d***	*AmPy* + *AmPy*HCl ***e***			*OXALATE* ***f***	*SUCCINATE* ***g***
SOLVENT		**METHANOL**					**SOLVENT**		**METHANOL**	
***t*/°C**	**%**						***t*/°C**	**%**		
10	50	(5.518)	(5.720)	(7.937)	8.436	9.116	25	39.14	[2.374]	
15	50	(5.506)	(5.697)	(7.916)	8.277	8.968	25	43.30		4.938
20	50	(5.498)	(5.680)	(7.898)	8.128	8.829	25	64		[5.398]
25	50	(5.493)	(5.666)	(7.884)	7.985	8.695	25	70	[2.771]	
30	50	(5.493)	(5.656)	(7.872)	7.850	8.570	25	84.20	3.358	
35	50	(5.496)	(5.650)	(7.863)	7.720	8.446	25	84.40		[6.289]
40	50	(5.502)	(5.648)	(7.858)	7.599	8.332	25	90	[3.729]	
							25	94.20		[7.147]
							25	94.29	4.133	
							25	100	(5.79)	(8.75)
Refs.		32-34			7	35	**Refs.**		36-38	

BUFFERS	*ACETATE* ***h***			*PHOSPHATE* ***i***			*TRIS* + ***d*** *TRIS*HCl	*SALICYLATE* ***j***	*BARBITURATE* ***k***			*OXALATE* ***l***	*SUCCINATE* ***g***
SOLVENT	**ETHANOL**									**SOLVENT**		**ETHANOL**	
% ***t*/°C**	10	20	40	10	20	40	50	100	100	***t*/°C**	**%**		
-10		5.075	5.498	7.376	7.638		8.912			25	30	2.298	4.668
-5	4.881	5.044	5.470	7.315	7.569		8.739			25	50	2.478	5.040
0	4.861	5.021	5.445	7.263	7.508		8.571			25	71.89	2.947	5.673
+5							8.411						
10							8.258						
15							8.114						
20							7.977						
25	4.822	4.967	5.395	7.104	7.310	7.597	7.845	(8.31)	(13.23)				
Refs.	34,39						2	37,40		**Refs.**		37,40	

BUFFERS	*TES* + Na*TES* ***m***		*PHOSPHATE* ***i***		*PHOSPHATE* ***n***			*CITRATE* ***o***	*PHOSPHATE* ***p***	*CARBONATE* ***q***
SOLVENT	**DIMETHYL SULFOXIDE**						**SOLVENT**	**DEUTERIUM OXIDE**		*****
% ***t*/°C**	20	30	20	30	20	30	**%** ***t*/°C**	100	100	100
-12		8.210					5	4.378	7.539	10.998
-5.5	7.889						10	4.352	7.504	10.924
0	7.649	7.860					15	4.329	7.475	10.855
+25	7.106	7.128	7.407	7.710	7.959	8.266	20	4.310	7.449	10.793
							25	4.293	7.428	10.736
							30	4.279	7.411	10.685
							35	4.268	7.397	10.638
							40	4.260	7.387	10.597
							45	4.253	7.381	10.560
							50	4.250	7.377	10.527
Refs.	30						**Refs.**	34,41		

LEGEND - ***a***: Acetic acid (0.05mol/kg) + Sodium acetate (0.05mol/kg) + NaCl (0.05mol/kg); ***b***: NaHSuccinate (0.05mol/kg) + NaCl (0.05mol/kg); ***c***: KH_2PO_4 (0.02mol/kg) + Na_2HPO_4 (0.02mol/kg) + NaCl (0.02mol/kg); ***d***: TRIS = Tris(hydroxymethyl)-methylamine (0.05mol/kg), TRISHCl = TRIS hydrochloride (0.05mol/kg); ***e***: AmPy = 4-Aminopyridine (0.06mol/kg), AmPyHCl = 4-Aminopyridinium chloride (0.06mol/kg); ***f***: Oxalic acid (0.01mol/kg) + Ammonium oxalate (0.01mol/kg); ***g***: Succinic acid (0.01mol/kg) + Lithium succinate (0.01mol/kg); ***h***: Acetic acid (0.05mol/kg) + Sodium acetate (0.05mol/kg); ***i***: KH_2PO_4 (0.025mol/kg) + Na_2HPO_4 (0.025mol/kg); ***j***: Salicylic acid (0.01mol/kg) + Lithium salicylate (0.01mol/kg); ***k***: Diethylbarbituric acid (0.01mol/kg) + Lithium diethylbarbiturate (0.01mol/kg); ***l***: Oxalic acid (0.01mol/kg) + Lithium oxalate (0.01mol/kg); ***m***: TES = Tris(hydroxymethyl) methylamino ethanesulphonic acid (0.070mol/kg) + NaTES = Sodium salt of TES (0.030mol/kg); ***n***: KH_2PO_4 (0.008695mol/kg) + Na_2HPO_4 (0.03043mol/kg); ***o***: $KD_2C_6H_5O_7$ (0.05mol/kg); ***p***: KD_2PO_4 (0.025mol/kg) + Na_2DPO_4 (0.025mol/kg); ***q***: $NaDCO_3$ (0.025mol/kg) + Na_2CO_3 (0.025mol/kg). For the buffers ***a***, ***b***, ***c***, ***d***, and ***e*** the original works furnish pH_{PS} values also at buffer molalities other than the mid molalities quoted above.

sults of White *et al.* (ref. 24) in the 50 percent mixture. However, these results are not completely consistent with the data for the 10, 20, 40 and 70 percent mixtures by Longhi *et al.* (refs. 12-14). Therefore, we do not quote $\mathrm{pH_{RVS}}$ results at 50% ethanol in Table 1, because of lack of conclusive information. Instead we recommend use of eq. (8) in order to calculate $\mathrm{pH_{RVS}}$ values.
The $\mathrm{pH_{PS}}$ of primary standards for the oxalate buffer and the succinate buffer (refs. 37,40) in 30 and 50 mass per cent ethanol (Table 2) have also been adjusted using the revised $E°$ values (ref. 14) obtained from eq. (7).
The 2-propanol/water mixtures (ref. 26) and the 1,2-ethanediol/water mixtures (refs. 1,44-47) shows similar features as those of the ethanol/water mixtures. Revised $E°$ values have been calculated and are represented by eqs. (9) and (10) (analogous to eq. (7)) as follows:

(for **2-propanol/water** mixtures):

$$(E°/T)\,/\,(\mathrm{V{\cdot}K^{-1}}) = 0.00074536 - 0.0008689x + 0.001239x^2 - 0.001974x^3 - 0.00013857u_1 + 0.002900u_1x - 0.02190u_1x^2 + 0.0294u_1x^3 - 0.00171u_2 - 0.0511u_2x + 0.307u_2x^2 - 0.464u_2x^3 \tag{9}$$

(for **1,2-ethanediol/water** mixtures (ref. 14)):

$$(E°/T)\,/\,(\mathrm{V{\cdot}K^{-1}}) = 0.00074521 - 0.00063982x + 0.00083383x^2 - 0.00085914x^3 - 0.0013585u_1 - 0.0018882u_1x + 0.0020060u_1x^3 - 0.0018800u_2 \tag{10}$$

Analogously to equation (8), the multilinear regression procedure mentioned above for the optimization of the reference value standards $\mathrm{pH_{RVS}}$ (i.e.,for the KHPh buffer) in the 2-propanol/water as well as in the 1,2-ethanediol / water mixtures hitherto studied (up to 70 mass per cent of organic cosolvent (ref. 3)) leads to equations (11) and (12), respectively:

(for **2-propanol/water** mixtures):

$$\mathrm{pH_{RVS}} = 4.0001 - 1.073x^{1/2} + 15.09x - 44.98x^2 + 51.89x^3 + 0.2910u_1 - 12.14u_1x + 31.13u_1x^2 + 12.53u_2 \tag{11}$$

(for **1,2-ethanediol/water** mixtures (ref. 14)):

$$\mathrm{pH_{RVS}} = 4.00292 + 4.04862x - 2.4506x^2 + 0.27845u_1 + - 2.753u_1x^2 + 5.744u_1x^3 + 65.39u_2 \tag{12}$$

In the recent $\mathrm{pH_{RVS}}$ determination for 2-methoxyethanol["methylcellosolve"] / water solvent mixtures (ref. 4), the $E°$ values recently redetermined critically by Vega, Barreto and Bates (ref. 48) were used, and for the $\mathrm{pH_{RVS}}$ results the following equation was formulated:

(for **2-methoxyethanol/water** mixtures):

$$\mathrm{pH_{RVS}} = 4.0033 + 9.901x - 17.87x^2 + 18.56\,x^3 + 0.353u_1 - 5.89u_1x + 16.81u_1x^3 + 8.83u_2 \tag{13}$$

The recommended $\mathrm{pH_{RVS}}$ data for pure water were reported earlier in a IUPAC document (ref. 42). Table 3 shows the $\mathrm{pD_{RVS}}$ data for heavy water, D_2O, calculated from the accurate e.m.f. measurement of Yung-Chi-Wu and Koch (ref. 31). These e.m.f. values satisfy the criterion mentioned above in that they were obtained by using the same electrode pair both for the determination of $E°$ and for that of $\mathrm{pD_{RVS}}$.

TABLE 3. - Values of pD-metric reference value standards ($\mathbf{pD_{RVS}}$) for the **0.05 mol·kg^{-1} Potassium Deuterium Phthalate (KDPh) buffer** in **Deuterium Oxide (D_2O)** at different temperatures t / °C, with overall estimated uncertainty δ.

t /°C	5	10	15	20	25	30	35	40	45	50
$\mathrm{pD_{RVS}}$	4.546	4.534	4.529	4.522	4.521	4.523	4.528	4.532	4.542	.552
δ	± 0.007									
Ref.	31									

However, a Debye-Hückel equation for $\gamma_{\pm DCl}$ with $a_0 = 0.41$ nm had originally been used for the evaluation of γ_{Cl}, equating γ_{Cl} to $\gamma_{\pm DCl}$ (ref. 31). Therefore, these data have now been recalculated along the Bates-Guggenheim convention for γ_{Cl} (*i.e.*, through eq. (22) of ref. 5), to put them in line with the IUPAC criteria (ref. 5).

General aspects of the pH_{RVS} values in aqueous organic solvent mixtures discussed in the present Report are summarized in Table 1. The pH_{RVS} data are now available for binary mixtures of water with *eight* organic solvents. This may allow upgrading and extending of the suggested procedure for predicting pH_{RVS} (refs. 28,43) for new, not so far studied, solvents. This prediction scheme could not be set up hitherto for the primary standards, pH_{PS}, because for any PS buffer solution values are available for no more than two organic solvents in admixture with water (Table 2). However, the recent published pH_{PS} results for the Tris+TrisHCl buffer in 50 mass per cent ethanol (ref. 2) may be symptomatic of reviving research interest in the area and justifying hopes for a rapid accumulation of appropriate data.

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