3.5 Practical measurement of pH in nonaqueous and mixed solvents

3.5.1 Introduction

Procedures analogous to those on which a practical pH scale for aqueous solutions have been based can be used to establish operational acidity scales in certain nonaqueous and mixed solvent media. A universal pH scale relating proton activity uniformly to the aqueous standard reference state is not possible, but separate scales for each medium can be achieved and will fulfill most of the requirements, such that the notional definition is ${}^{s}_{s}pH = -\log(m_H\,{}^{s}_{s}\gamma_{m,H})$, where ${}^{s}_{s}\gamma_{m,H}$ is referred to the standard state in each particular medium s. The 'normal scale length of pH' in each solvent and solvent mixture is determined by the autoprotolysis constant (see section 3.2.3.5).

3.5.2 Notation and terminology

The notation adopted is that used by Robinson and Stokes for their discussion of the effect of the medium on transferring a binary electrolyte from water (w) to a nonaqueous or mixed solvents. Thus, lower-case left-hand superscripts indicate the solvent (w or s) in which measurements are being made; lower-case left-hand subscripts indicate the solvent in which the ionic activity coefficient γ is referred to unity at infinite dilution (w or s).

Therefore, the potential of the hydrogen electrode (at 101 325 Pa pressure of H_2) as a function of the activity a_H of the H^+ ion in the solvent s is expressed as:

$$ {}^{s}E_H = {}^{s}E^{o}_{H} + k\,\lg({}^{s}_{s}\gamma_H m_H/m^{o}) = {}^{s}E^{o}_{H} + k\,\lg({}^{s}_{s}a_H) = {}^{s}E^{o}_{H} - k({}^{s}_{s}pH) \qquad 3.27 $$

where k = (RT/F) ln 10, the concentration is on the molality scale m, and the ionic charge is omitted in the subscripts; and analogously:

$$ {}^{w}E_H = {}^{w}E^{o}_{H} + k\,\lg({}^{w}_{w}\gamma_H m_H/m^{o}) = {}^{w}E^{o}_{H} + k\,\lg({}^{w}_{w}a_H) = {}^{w}E^{o}_{H} - k({}^{w}_{w}pH) \qquad 3.28 $$

in water. It is to be noted that ${}^{s}E^{o}_{H}$ and ${}^{w}E^{o}_{H}$ are standard electrode potentials (or, in other words, potentials determined with respect to an electrode of ideally invariant standard potential in the various solvents). Also, the notation ${}^{s}_{w}\gamma^{o}_{H}$ (corresponding to the notation ${}_{m}\gamma_H$ sometimes used by Bates) will be used for the primary medium effect (related to the standard Gibbs energy change) for the transfer of the H^+ ion from water (w) to the solvent s (nonaqueous or mixed). Thus the ${}^{s}_{s}pH$ value measured in the solvent s relating to the pH scale specific to the solvent s might be expressed as ${}^{s}_{w}pH$ on an "intersolvental" scale with ultimate reference to the solvent water w, and be meaningfully compared with the latter by the following conversion equation:

$$ {}^{s}_{w}pH = -\lg({}^{s}_{w}\gamma_H m_H/m^{o}) = {}^{s}_{s}pH - \lg({}^{s}_{w}\gamma^{o}_{H}) = {}^{s}_{s}pH + ({}^{w}E^{o}_{H} - {}^{s}E^{o}_{H})/k \qquad 3.29 $$

where:

$$ {}^{s}_{w}\gamma_H = {}^{s}_{s}\gamma_H \times {}^{s}_{w}\gamma^{o}_{H} \text{ and } {}^{s}_{w}\gamma^{o}_{H} \rightarrow 1 \text{ as } s \rightarrow w \qquad 3.30 $$

The feasibility of the pH scale is hindered by the indeterminability of the (${}^{w}E^{o}_{H}$ - ${}^{s}E^{o}_{H}$) term.

In conclusion, taking into account that simple and functional symbols (e.g. E_x, the e.m.f. of operational cell (XI) measured on the sample solution at unknown pH_x; E_s, E_{s1}, E_{s2}..., the e.m.f.'s of operational cell (XII) measured on standard solutions at known pH_s, pH_{s1}, pH_{s2}...) are currently in use with the operational equations for pH measurements in aqueous solutions, any solvent indication (s and/or w) is better placed (as superscripts and/or subscripts) on the left-hand of the relevant quantities, as in Robinson and Stokes' notation. However, the simple symbol γ_t, and the related term "transfer activity coefficient" proposed by Trémillon and Coetzee, can also be recommended instead of the cumbersome symbol ${}^{s}_{w}\gamma^{o}_{H}$, provided that γ_t is explicitly and unambiguously defined each time. The quantity γ_t can also be used to represent the analogous transfer property for ions other than H^+ between solvents.

3.5.3 Operational cells and equations

Just as in the case of aqueous solutions, the notional definition of pH in a solvent s is:

$$ {}^{s}_{s}pH = p({}^{s}_{s}a_H) = -\lg({}^{s}_{s}\gamma_H m_H) \qquad 3.31$$

where ${}^{s}_{s}a_H$ is the activity of the single H^+ ion at the molal concentration m_H and ${}^{s}_{s}\gamma_H$ is the corresponding single-H^+-ion activity coefficient, and the quantity ${}^{s}_{s}\gamma_H$ is, in strict thermodynamic terms, immeasurable. For this reason, as for the aqueous ${}^{w}_{w}pH$ standardisation, ${}^{s}_{s}pH$ is defined *operationally*, namely, in terms of the operation or method used to determine it. This method consists of measuring the e.m.f. ${}^{s}E_x$ of the cell (XI), (compare cell (II)):

Reference electrode	Salt bridge in solvent s	sample solution at unknown ${}^{s}_{s}pH_x$ in solvent s	H^+-sensing electrode	(XI)

(which is the **operational cell**). ${}^{s}E_x$ is a linear function of the unknown ${}^{s}_{s}pH_x$ according to the Nernstian relation:

$$ {}^{s}E_x = {}^{s}E^{o} - k({}^{s}_{s}pH_x) + {}^{s}E_{jx} \qquad 3.32$$

where ${}^{s}E^{o}$ is a temperature dependent constant, and ${}^{s}E_{jx}$ is the liquid junction potential arising at the junction between the sample solution and the salt bridge (which is *assumed* to be negligible if the salt bridge is a solution of an equi-transferent binary salt in the *same solvent* s of, and at *much higher concentration* than, the sample solution at ${}^{s}_{s}pH_x$). Since ${}^{s}E^{o}$ is unknown, determining ${}^{s}_{s}pH_x$ from the measured ${}^{s}E_x$ requires cell calibration by a standard solution of assigned ${}^{s}_{s}pH_s$ (see 3.5.4 for the determination of ${}^{s}_{s}pH_s$), which requires replacing the sample solution at ${}^{s}_{s}pH_x$ in cell (XI) by the standard solution at ${}^{s}_{s}pH_s$ and measuring the e.m.f. ${}^{s}E_s$ of the resulting cell (XII):

Reference electrode	Salt bridge in solvent s	sample solution at unknown ${}^{s}_{s}pH_{s}$ in solvent s	H^{+} -sensing electrode	(XII)

having the same H^{+}-sensing electrode, reference electrode and salt bridge of cell (XI) at the same temperature and pressure. As the Nernst expression for ${}^{s}E_{s}$ is:

$$ {}^{s}E_{S} = {}^{s}E^{o} - k({}^{s}_{s}pH_{S}) + {}^{s}E_{JS} \qquad 3.33 $$

then ${}^{s}_{s}pH_{X}$ is determinable in terms of the assigned standard ${}^{s}_{s}pH_{S}$ by:

$$ {}^{s}_{s}pH_{X} = {}^{s}_{s}pH_{S} - ({}^{s}E_{X} - {}^{s}E_{S})/k \qquad 3.34 $$

(which is the pH *operational equation* in the solvent s) ignoring the term:

$$ {}^{s}\Delta E_{J} = {}^{s}E_{JX} - {}^{s}E_{JS} \qquad 3.35 $$

known as the *residual liquid junction potential.* When there is a well-founded suspicion that ${}^{s}\Delta E_{J}$ cannot be neglected (e.g. for possible inappropriateness, or ineffectiveness, of the salt bridge chosen), the error in ${}^{s}_{s}pH_{X}$ caused by ${}^{s}\Delta E_{J}$ can be reasonably reduced by the procedure of *bracketting unknown and standards,* namely, measuring *two* emf's, ${}^{s}E_{S1}$ and ${}^{s}E_{S2}$ of cell (XII) with the two respective standards, ${}^{s}_{s}pH_{S1}$ and ${}^{s}_{s}pH_{S2}$, one lower and the other higher than (and as close as possible to) the unknown ${}^{s}_{s}pH_{X}$. In such case the operational equation becomes:

$$ {}^{s}_{s}pH_{X} = {}^{s}_{s}pH_{S1} + ({}^{s}E_{X} - {}^{s}E_{S1})({}^{s}_{s}pH_{S2} - {}^{s}_{s}pH_{S1})/({}^{s}E_{S2} - {}^{s}E_{S1}) \qquad 3.36 $$

3.5.4 Assignment of the reference value standard ${}^{s}_{s}pH_{S}$

The RVS material selected for making up the ${}^{s}_{s}pH_{S}$ standard in the domain of the solvent mixtures s with water at 100 down to~~10 wt per cent water is the 0.05 mol/kg potassium hydrogen phthalate (KHPh) buffer solution in s.

The procedure for the determination of the relevant ${}^{s}_{s}pH_{S}$ values for the RVS, in general, follows the same scheme used for the RVS in water, and is based on measuring the e.m.f. ${}^{s}E$ of a cell without liquid junction, at fixed m_{S} but varying m_{1}:

Electrode reversible to H^{+} in solvent s	RVS buffer (m_{S}) + KX (m_{1}) in solvent s	Electrode reversible to X^{-} in solvent s	(XIII)

For most aquo-organic mixed solvents s (and also for some 100%-pure nonaqueous solvents) the cell (XIII) takes the form:

Pt | H_2 (101 325 Pa) | KHPh (m_{S}) + KCl (m_{Cl}) | AgCl | Ag | Pt (XIV) where m_S is 0.05 mol/kg and m_{Cl} is varied.

From the e.m.f. expression (see 3.16):

$$- \lg ({}^s_s a_H \, {}^s_s\gamma_{Cl} m_{Cl}/m^o) = ({}^sE - {}^sE^o)/k + \lg (m_{Cl}/m^o) \qquad 3.37$$

where ${}^sE°$ is the standard e.m.f. of cell (XIII), k =(RT/F)ln10, and the subscript ions are indicated without charge to simplify printing, it is clear that:

(i) knowledge of accurate ${}^sE°$ values is essential;

(ii) an extrathermodynamic assumption, i.e. a Debye-Hückel equation of the type (see equation 3.09):

$$\lg \gamma_{Cl} = - AI^{½}/(1 + BaI^{½}) \qquad 3.38$$

is necessary to compute the single Cl^-–ion activity coefficient ${}^s_s\gamma_{Cl}$ in order to obtain the non-thermodynamic quantity ${}^s_s$pH from the thermodynamic quantity p(${}^s_s a_H \, {}^s_s\gamma_{Cl}$).

The equation (3.38), where I is the total ionic strength of the mixed electrolyte KHPh + KCl, introduces two features:

(iii) one can write I = I_S + m_{Cl}, where I_S is the ionic strength of KHPh alone, but $I_S \neq m_S$ depending on the ionization constants of the *o*-phthalic acid H_2Ph: this implies iterative calculation procedures to obtain I_S, I and ultimately γ_{Cl};

(iv) the ion-size parameter a is assigned a value fixed by the Bates-Guggenheim convention extended to the general solvent s by the relation, at each temperature T

$$({}^sB\,{}^sa)_T = 1.5 \{{}^w\varepsilon \, {}^w\rho/({}^s\varepsilon \, {}^w\rho)\}^{1/2}_T \qquad 3.39$$

where ${}^sB$ is the Debye-Hückel constant of eq. (3.38), appropriate to the (single or mixed) solvent s, ${}^w\varepsilon$ and ${}^s\varepsilon$ are the relative permittivities of pure water (superscript ^{w}) and of the solvent (superscript ^{s}), and ${}^w\rho$ and ${}^s\rho$ are the corresponding densities. If s is water, equation (3.39) reduces to Ba = 1.5, which is the form of the Bates-Guggenheim convention which was introduced originally for pH standardisation in pure water.

The equations (3.37) to (3.39) are combined into an extrapolation function Φ to determine pH_{RVS} as intercept at m_{Cl} = 0 of a linear regression plot of Φ *vs.* m_{Cl}, with optimization of pH_{RVS} through iterative calculation cycles. In this context, another important point must be outlined:

(v) the above determination and optimization of pH_{RVS} must be carried out at *each* distinct composition of the solvent s, this composition being usually expressed as the mol fraction x of the *nonaqueous* component.

In fact, even a minimal change in x causes a change in the standard state "hyp. m = 1" for the H^+ ion (*primary medium effect* upon H^+), and also a change in both the pH scale and its position relative to the familiar aqueous pH scale. Therefore, each pH_{RVS}, so determined in a solvent s, is only valid for the pH scale in *that* solvent. It was shown that the above determination and optimization of pH_{RVS} at each composition x of the solvent can be carried out by single-stage multilinear regression of E as a function of m_{Cl}, x, and temperature T, giving final, smoothed, recommended values. This is very important because there might be various independent E sets from different authors with obvious problems of overlapping and resulting difficulties in extracting best values. The same applies for the determination of the standard e.m.f. E° of cell (XIV), required by eq. (3.37), which is currently carried out by the classical method of extrapolating to I=0 a suitable function of the e.m.f. of the cell:

Pt | H_2 (101 325 Pa) | HCl (m) in solvent s | AgCl | Ag | Pt (XV)

3.5.5 Recommended values of pH_{RVS} and pH_S

All the reference value standards (pH_{RVS}) and primary standards (pH_S) determined to date have been re-examined to ensure compliance with the above IUPAC rules and to provide sets of recommended data. These have been grouped in three Tables, of which Table 3.5.1 reports the data (pH_{RVS}) which are relevant to the RVS buffer (the 0.05 m potassium hydrogen phthalate buffer) in various aqueous organic solvent mixtures. Table 3.5.2 reports values (pD_{RVS}) that pertain to the special case of the RVS buffer (0.05 m potassium deuterophthalate buffer (KDPh) for pD in heavy water, D_2O, and Table 3.5.3 collects those for such other buffers as acetate, oxalate, carbonate, succinate, phosphate, Tris + Tris.HCl, *etc*, in single or mixed solvents (including heavy water, D_2O) and at various temperatures. In the case of ethanol/water and dimethylsulphoxide/water mixtures, the Celsius temperature range extends to subzero.

TABLE 3.5.1 Values of pH Reference Value Standards (pH_{RVS}) for the 0.05 m potassium hydrogen phthalate (KHPh) buffer in various aqueous organic solvent mixtures (mol fraction x) at different temperatures t/°C, with overall estimated uncertainties δ.

	Weight percent of the nonaqueous solvent in mixtures with water									
	5	10	15	20	30	40	50	64	70	84.2
METHANOL										
x		0.0588		0.1232			0.3599	0.4999		0.7498
t/°C										
10		4.254		4.490			5.151	5.488		6.254
25		4.243		4.468			5.125	5.472		6.232
40		4.257		4.472			5.127	5.482		6.237
δ					±0.003					
ETHANOL										
x		0.0416		0.0891		0.2068			0.4771	
-5		4.266		4.570		5.112			5.527	
0		4.249		4.544		5.076			5.500	
10		4.235		4.513		5.026			5.469	
25		4.236		4.508		4.976			5.472	
40		4.260		4.534		4.978			5.493	
δ		±0.002		±0.003		±0.002			±0.002	
2-PROPANOL										
x		0.0322			0.1138		0.2305		0.4115	
15		4.238			4.889		5.217		5.514	
25		4.242			4.849		5.186		5.499	
35		4.251			4.836		5.204		5.541	
45		4.274			4.830		5.191		5.587	
δ		±0.005			±0.002		±0.006		±0.013	
ACETONITRILE										
x	0.0226		0.0719		0.1583		0.3050		0.5059	
15	4.163		4.533		5.001		5.456		6.159	
25	4.166		4.533		5.000		5.461		6.194	
35	4.178		4.542		5.008		5.475		6.236	
δ					±0.005					
1,4-DIOXANE										
x		0.0222			0.0806		0.1697			
15		4.330			5.034		5.779			
25		4.329			5.015		5.782			
35		4.337			5.007		5.783			
45		4.355			5.008		5.783			
δ					±0.002					
DIMETHYLSULPHOXIDE										
x				0.0545	0.0899					
-12					4.870					
25				4.471	4.761					
δ					±0.002					

TABLE 3.5.2 Values of pD Reference Value Standards (pD_{RVS}) for the 0.05 m potassium deutero phthalate (KDPh) buffer in deuterium oxide (D_2O) at various temperatures t/°C, with overall estimated uncertainty $\delta = \pm 0.007$.

t/°C	5	10	15	20	25
pD_{RVS}	4.546	4.534	4.529	4.522	4.521
t/°C	30	35	40	45	50
pD_{RVS}	4.523	4.528	4.532	4.542	4.552

TABLE 3.5.3 Values of primary standards (pHS) for pH measurements in different solvents or aqueous organic solvent mixtures at various temperatures. Values not fully complying with the IUPAC criteria are quoted in parentheses (); values not satisfying F-tests are quoted in braces {}. All % values for mixed solvents with water are by weight.

Methanol 50%					
t/°C	Acetate	Succinate	Phosphate	Tris+Tris.HCl	AmPy+AmPh.HCl
	a	*b*	*c*	*d*	*e*
10	(5.518)	(5.720)	(7.937)	8.436	9.11
15	(5.506)	(5.697)	(7.916)	8.277	8.968
20	(5.498)	(5.680)	(7.898)	8.128	8.829
25	(5.493)	(5.666)	(7.884)	7.985	8.695
30	(5.493)	(5.656)	(7.872)	7.850	8.570
35	(5.496)	(5.650)	(7.863)	7.720	8.446
40	(5.502)	(5.648)	(7.858)	7.599	8.332

	Oxalate	Succinate	Oxalate	Succinate	Salicylate	Barbiturate
	g	*h*	*f*	*h*	*i*	*j*
%(m/m)	Methanol at 25°C		Ethanol at 25°C			
0	{2.145}	{4.119}	2.146	4.113		
30			2.312	4.691		
39.14	{2.374}					
43.30		4.938				
50			2.506	5.073		
64		{5.398}				
70	{2.771}					
71.89			2.985	5.713		
84.20	3.358					
84.40		{6.289}				
90	{3.729}					
94.20		{7.147}				
94.29	4.133					
100	(5.79)	(8.75)			(8.31)	(13.23)

	Acetate *k*					Phosphate *l*			
		Ethanol					Ethanol		
t/°C	H_2O	10%	20%	40%	t/°C	H_2O	10%	20%	40%
-10			5.075	5.498	-10		7.376	7.638	
-5		4.881	5.044	5.470	-5		7.315	7.569	
0	4.687	4.861	5.021	5.445	0	6.984	7.263	7.508	
25	4.670	4.822	4.967	5.395	25	6.865	7.104	7.310	7.597

TABLE 3.5.3 (continued)

	Citrate *n*	Phosphate *o*	Carbonate *p*
t/°C	D_2O*	D_2O*	D_2O*
5	4.378	7.539	10.998
10	4.352	7.504	10.924
15	4.329	7.475	10.855
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

Phosphate *l*			
t/°C	H_2O	DMSO 20%	DMSO 30%
25	6.865	7.407	7.710

Phosphate *m*			
t/°C	H_2O	DMSO 20%	DMSO 30%
25	7.413	7.959	8.266

Tes + NaTes *q*			
t/°C	H_2O	DMSO 20%	DMSO 30%
-12			8.210
-5.5		7.889	
0	7.558	7.649	7.860
25	7.026	7.106	7.128

a: Acetic acid (0.05 m) + Sodium acetate (0.05 m) + NaCl (0.05 m)
b: NaHSuccinate (0.05 m) + NaCl (0.05 m)
c: KH_2PO_4 (0.02 m) + Na_2HPO_4 (0.02 m) + NaCl (0.02 m)
d: Tris = Tris (hydroxymethyl)aminomethane (0.05 m);
Tris.HCl = TRIS hydrochloride (0.05 m)
e: AmPy = 4-Aminopyridine (0.06 m);
AmPy.HCl = 4-Aminopyridinium chloride (0.06 m)
f: Oxalic acid (0.01 m) + Lithium oxalate (0.01 m)
g: Oxalic acid (0.01 m) + Ammonium oxalate (0.01 m)
h: Succinic acid (0.01 m) + Lithium succinate (0.01 m)
i: Salicylic acid (0.01 m) + Lithium salicylate (0.01 m)
j: Diethylbarbituric acid (0.01 m) + Lithium diethylbarbiturate (0.01 m)
k: Acetic acid (0.05 m) + Sodium acetate (0.05 m)
l: KH_2PO_4 (0.025 m) + Na_2HPO_4 (0.025 m)
m: KH_2PO_4 (0.008695 m) + Na_2HPO_4 (0.03043 m)
n: $KD_2C_6H_5O_7$ (0.05 m)
o: KD_2PO_4 (0.025 m) + Na_2DPO_4 (0.025 m)
p: $NaDCO_3$ (0.025 m) + Na_2CO_3 (0.025 m)
q: Tes = N-tris(hydroxymethyl)methyl-2-aminoethane sulfonic acid (0.07 m)
+NaTes = Sodium salt of TesES (0.03 m).

For the buffers a,b,c,d,e the original works give pH_s values from 0.005, 0.005, 0.002, 0.01, 0.02 m to 0.05, 0.05, 0.02, 0.10,0.10 m at 0.005, 0.005, 0.002, 0.01, 0.02 intervals, respectively.
* The standard values in heavy water (D_2O) are in terms of pD_s.