Pure & Appl. Chem., Vol. 57, No. 6, pp. 865–876, 1985.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

CRITERIA FOR STANDARDIZATION OF pH MEASUREMENTS in Organic Solvents and Water + Organic Solvent Mixtures of Moderate to High Permittivities

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Criteria for standardization of pH measurements in organic solvents and water + organic solvent mixtures of moderate to high permittivities

1. INTRODUCTION

pH standardisation in aqueous solutions may now be considered as substantially achieved (refs. 1,2).

The experimental work done so far in pioneering pH standardisation in nonaqueous and mixed solvents – an extension which is very important for chemistry and chemical engineering –, though based on sound physicochemical principles (refs.3,3a), is regrettably fragmentary and scarce. Systematic acquisition of data is urgently needed for many important media, although the field is apparently almost unlimited. Doing this without valid and recognised objectives might clearly result in a disorienting and chaotic situation. For this standardisation to be complete and effective it would ideally embrace the following features:

1.1 To define the "normal scale length of pH" in each, nonaqueous or mixed, solvent considered, for obvious comparison purposes. This requires knowledge of the autoprotolysis constant K_{ap} (in fact, $-\log K_{ap}$ = normal scale length of pH (ref.4)) pertaining to each solvent considered, which can be achieved by appropriate thermodynamic methods.

1.2 To define as many pH standards, pH_S , as necessary to cover the normal scale length of pH in each solvent, within the usual range of temperatures. This requires the appropriate experimental work and an extra-thermodynamic procedure, which is a logical extension (refs.3, 3a,5) of what is now endorsed, and currently applied, in the case of aqueous solutions.

1.3 To have the above normal scale lengths of pH defined (with the appropriate acidic and alkaline ends) with ultimate reference to water (because of the obvious and indisputable key role of water with respect to any other solvent, or solvent mixture with water itself), so as to constitute one "intersolvental" scale of pH which would provide physically interrelated and comparable pH data.

However, the extrathermodynamic step implied by point 1.3 for the determination of the primary medium effect ($_{w}^{s}\gamma_{H}^{o}$, see point 2.3) for the transfer of the H^+ ion (refs.3-6) from water to the solvent considered (note that $-\log {}_{w}^{s}\gamma_{H}^{o}$ is the acidic end of the normal scale length of pH in the solvent s with reference to water w (ref.4)) has not hitherto attained sufficient convergency of results or consensus of opinion: therefore, systematic acquisition of final $_{w}^{s}\gamma_{H}^{o}$ data is prevented and the desirable objective 1.3 cannot be attained, for the present at least. In this context attention is drawn to the recent IUPAC documents on standard Gibbs energies of transfer of single ions (ref.6a) and on intercomparison of standard electrode potentials in nonaqueous solvents (ref.7).

The objective of the present document is thus limited to point 1.2 .

2. SOLVENT COMPOSITION

Measuring the pH of solutions in 100%-pure nonaqueous solvents is only occasionally performed. The real, fundamental demand is for the availability of precise standard pH_S data for an appropriate reference value standard (RVS), or primary standard, in binary solvent mixtures water/nonaqueous co-solvent with the water proportion varying from 100% to some few per cent. This constitutes a nearly unlimited domain, where the obvious continuity and smooth progressiveness of parameters upon increasing the proportion of nonaqueous co-solvent in admixtures

with water make it feasible and highly recommendable to select only one buffer substance for the preparation of the RVS solutions in the various solvent mixtures and the assignment of the respective pH_S values.

2.1 THE REFERENCE VALUE STANDARDS OF pH IN SOLVENT MIXTURES WITH WATER

The qualities of potassium hydrogen phthalate (KHPh) as the most studied (refs.8-14) among the pH reference materials both in aqueous and mixed solvents designate it as the most appropriate RVS substance in solvent mixtures with 100% down to about 10% water proportions (see 2.2). By extension of the experimental conditions already standardised in water (refs.1,11), as well as in water/dimethylsulfoxide (ref.12), water/methanol (ref.13), and water/1,4-dioxane (ref. 14), the operative concentration m_S of KHPh is fixed as m_S = 0.05 mol/kg.

2.2 SUBSIDIARY REFERENCE VALUE STANDARDS OF pH IN WATER-POOR SOLVENT MIXTURES

It is unlikely that KHPh can be adopted as the RVS solution in *all* the possible water-poor solvent mixtures approaching 100% nonaqueous co-solvent, *e.g.* possibly because of restricted solubility. It is, moreover, well known that the response of the usual H^+-sensing electrodes often becomes problematic, if it exists at all, when the last traces of water are removed from solvent mixtures with certain co-solvents where, *inter alia*, it would be rather difficult to assess protolytic equilibria susceptible of pH-metric standardisation. Thus it appears reasonable that, for the domain of 90 to 100%-pure nonaqueous solvents, pH standardisation – possibly selecting appropriate subsidiary RVS if KHPh were inapplicable – be deferred until the relevant physico-chemical parameters be completely understood.

2.3 NOTATION AND TERMINOLOGY

The notation adopted in this document is based on that used by Robinson and Stokes for their discussion of the medium effect upon transferring a binary electrolyte from water (w) to a nonaqueous or mixed solvent (ref.15). Thus, lower-case left-hand superscripts indicate the solvent (w or s) where measurements are being made; lower-case left-hand subscripts indicate that the ionic activity coefficient γ_i is referred to unity at infinite dilution in that solvent (w or s).

Therefore, the potential of the hydrogen electrode (at 1 atm pressure of H_2) as a function of the activity a_H of the H^+ ion in the solvent s is expressed as:

$$ {}^{s}E_H = {}^{s}E^{\circ}_H + k\log({}^{s}_{s}\gamma_H m_H) = {}^{s}E^{\circ}_H + k\log({}^{s}_{s}a_H) = {}^{s}E^{\circ}_H - k({}^{s}_{s}\mathrm{pH}) \qquad (1) $$

where $k = (RT/F)\ln 10$, the concentration is on the molal scale m, the ionic charge is omitted in the subscrips, and use is made of the contracted notation p = -log; and, analogously:

$$ {}^{w}E_H = {}^{w}E^{\circ}_H + k\log({}^{w}_{w}\gamma_H m_H) = {}^{w}E^{\circ}_H + k\log({}^{w}_{w}a_H) = {}^{w}E^{\circ}_H - k({}^{w}_{w}\mathrm{pH}) \qquad (2) $$

in water. It is to be noted that ${}^{s}E^{\circ}_H$ and ${}^{w}E^{\circ}_H$ are absolute (true) standard electrode potentials (or, in other words, potentials determined with respect to an electrode of ideally invariant standard potential in the various solvents). Also, by the ${}^{s}_{w}\gamma^{\circ}_H$ notation (corresponding to the notation ${}_{m}\gamma_H$ sometimes used by Bates (ref.16)) will be meant the primary medium effect (namely, the standard Gibbs energy change) for the transfer of the H^+ ion from water (w) to the solvent s (nonaqueous or mixed). Thus the ${}^{s}_{s}\mathrm{pH}$ value measured in the solvent s and quoted on the pH scale specific to the said solvent s (see 2.4) might be expressed as ${}^{s}_{w}\mathrm{pH}$ on one "intersolvental" scale with ultimate reference to the solvent water w – and be meaningfully compared with the latter – by the following conversion equation:

$$ {}^{s}_{w}\mathrm{pH} = -\log({}^{s}_{w}\gamma_{H} m_{H}) = {}^{s}_{s}\mathrm{pH} - \log({}^{s}_{w}\gamma^{o}_{H}) = {}^{s}_{s}\mathrm{pH} + ({}^{w}E^{o}_{H} - {}^{s}E^{o}_{H})/k \qquad (3) $$

whereby:

$$ {}^{s}_{w}\gamma_{H} = {}^{s}_{s}\gamma_{H} \times {}^{s}_{w}\gamma^{o}_{H} \quad \text{and} \quad {}^{s}_{w}\gamma^{o}_{H} \longrightarrow 1 \text{ as } s \longrightarrow w \qquad (4) $$

The feasibility of the ${}^{s}_{w}\mathrm{pH}$ scale, which is hindered by the indeterminability of the $({}^{w}E^{o}_{H} - {}^{s}E^{o}_{H})$ term, has been already commented on in connexion with point 1.3 .

In conclusion, taking into account that simple and functional symbols (*e.g.* E_X, emf of operational cell (6) measured on the sample solution at unknown pH_X; E_S, E_{S1}, $E_{S2}\ldots$, emf's of operational cell (8) measured on standard solutions at known pH_S, pH_{S1}, $\mathrm{pH}_{S2}\ldots$) are currently in use with the operational equations already endorsed for pH measurements in aqueous solutions, any solvent indication (s and/or w) is best placed (as superscripts and/or subscripts) on the left-hand of the relevant quantities, just as in Robinson and Stokes' notation (ref.15). However, the simple symbol γ_t and the related term "transfer activity coefficient" proposed by Trémillon and Coetzee (ref.16a) can well be finally recommended here in lieu of the somewhat cumbersome symbol ${}^{s}_{w}\gamma^{o}_{H}$, provided that γ_t is explicitly and unambiguously defined in each new publication. For γ_t might be also used to represent the analogous transfer property for ions other than H^+ in several different solvents dealt with in the same paper.

2.4 OPERATIONAL CELLS AND EQUATIONS

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

$$ {}^{s}_{s}\mathrm{pH} = \mathrm{p}({}^{s}_{s}a_{H}) = -\log({}^{s}_{s}\gamma_{H} m_{H}) \qquad (5) $$

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, implies that the quantity ${}^{s}_{s}\gamma_{H}$ is – in strict thermodynamic terms – immeasurable (refs.17-21). For this reason, as was done for the aqueous ${}^{w}_{w}\mathrm{pH}$ standardisation (refs.1,22,23), ${}^{s}_{s}\mathrm{pH}$ is defined *operationally*, namely, in terms of the operation or method used to determine it. This method consists of measuring the electromotive force (emf) ${}^{s}E_X$ of the cell:

Reference electrode	Salt bridge in solvent s	Sample solution at unknown ${}^{s}_{s}\mathrm{pH}_X$ in solvent s	H^+-sensing electrode

(6)

(which is called the *operational cell*) because ${}^{s}E_X$ is a linear function of the unknown ${}^{s}_{s}\mathrm{pH}_X$ according to the Nernstian relation:

$$ {}^{s}E_X = {}^{s}U - k({}^{s}_{s}\mathrm{pH}_X) + {}^{s}E_{JX} \qquad (7) $$

where ${}^{s}U$ 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 (and is *assumed* to be negligible if the salt bridge is a solution of an equitransferent binary salt in the *same solvent* s of, and at *much higher concentration* than, the sample solution at ${}^{s}_{s}\mathrm{pH}_X$). Since ${}^{s}U$ is unknown, determining ${}^{s}_{s}\mathrm{pH}_X$ from the measured ${}^{s}E_X$ requires cell calibration by a standard solution of assigned ${}^{s}_{s}\mathrm{pH}_S$ (see point 2.5 for the determination of ${}^{s}_{s}\mathrm{pH}_S$), which implies replacing the sample solution at ${}^{s}_{s}\mathrm{pH}_X$ in cell (6) by the standard solution at ${}^{s}_{s}\mathrm{pH}_S$ and measuring the emf ${}^{s}E_S$ of the resulting cell (8):

Reference electrode	Salt bridge in solvent s	Standard solution at known ${}^{s}_{s}\mathrm{pH}_S$ in solvent s	H^+-sensing electrode

(8)

having the same H^+-sensing electrode, reference electrode and salt bridge of cell (6) at the

same temperature and pressure. As the Nernstian expression for ${}^{s}E_S$ is:

$$ {}^{s}E_S = {}^{s}U - k({}^{s}_{s}\mathrm{pH}_S) + {}^{s}E_{JS} \tag{9} $$

then ${}^{s}_{s}\mathrm{pH}_X$ is determinable in terms of the assigned standard ${}^{s}_{s}\mathrm{pH}_S$ by:

$$ {}^{s}_{s}\mathrm{pH}_X = {}^{s}_{s}\mathrm{pH}_S - ({}^{s}E_X - {}^{s}E_S)/k \tag{10} $$

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

$$ {}^{s}\Delta E_J = {}^{s}E_{JX} - {}^{s}E_{JS} \tag{11} $$

which is called 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 ${}^{s}_{s}\mathrm{pH}_X$ 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 (8) with the two respective standards, ${}^{s}_{s}\mathrm{pH}_{S1}$ and ${}^{s}_{s}\mathrm{pH}_{S2}$, one lower and the other higher than (and as close as possible to) the unknown ${}^{s}_{s}\mathrm{pH}_X$. In such case the operational equation becomes:

$$ {}^{s}_{s}\mathrm{pH}_X = {}^{s}_{s}\mathrm{pH}_{S1} + ({}^{s}E_X - {}^{s}E_{S1})({}^{s}_{s}\mathrm{pH}_{S2} - {}^{s}_{s}\mathrm{pH}_{S1})/({}^{s}E_{S2} - {}^{s}E_{S1}) \tag{12} $$

2.5 ASSIGNMENT OF THE REFERENCE VALUE STANDARD ${}^{s}_{s}\mathrm{pH}_S$

For the reasons discussed under 2.1 the RVS material selected for making up the ${}^{s}_{s}\mathrm{pH}_S$ 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 hydrogenphthalate buffer solution in s.

The procedure for the determination of the relevant ${}^{s}_{s}\mathrm{pH}_S$ values for the RVS, in general, follows the same scheme used for the RVS in water, and is based on measuring the emf ${}^{s}E$ of a cell without liquid junction, of the type (13), 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	(13)

For most aquo-organic mixed solvents s (and also for some 100%-pure nonaqueous solvents) the cell (13) takes the form:

Pt | H_2 (1 atm)	KHPh (m_S) + KCl (m_1) in solvent s	AgCl | Ag | Pt	(14)

Let us consider first the case where the relative permittivity (dielectric constant) of the solvent is sufficiently high to make the ion association negligible.

A solution of KHPh of concentration m_S has an ionic strength $I_S \neq m_S$, due to the ionisation constants of the parent *o*-phthalic acid H_2Ph, therefore, for the total ionic strength I of the mixed electrolyte KHPh + KCl in cell (14), one can write $I = I_S + m_1$. Inspection of the expression of the emf of the cell (14):

$$ ({}^{s}E - {}^{s}E^{\circ})/k = \mathrm{p}({}^{s}_{s}a_{\mathrm{H}\,s}{}^{s}\gamma_{\mathrm{Cl}}) + \mathrm{p}m_1 = {}^{s}_{s}\mathrm{pH} + \mathrm{p}({}^{s}_{s}\gamma_{\mathrm{Cl}}) + \mathrm{p}m_1 \tag{15} $$

makes it clear that the quantity:

$$ \mathrm{p}({}^{s}_{s}a_{\mathrm{H}\,s}{}^{s}\gamma_{\mathrm{Cl}}) = ({}^{s}E - {}^{s}E^{\circ})/k - \mathrm{p}m_1 \tag{16} $$

is determinable in thermodynamically exact terms. An extrathermodynamic assumption – the Debye-Hückel equation (refs.24,25) – is, however, now necessary to compute the single-Cl^--ion activity coefficient term:

$$ \mathrm{p}({}^{s}_{s}\gamma_{\mathrm{Cl}}) = {}^{s}AI^{\frac{1}{2}}/(1 + {}^{s}a_0{}^{s}BI^{\frac{1}{2}}) \tag{17} $$

which depends on the total ionic strength $I = I_S + m_1$ of the KHPh + KCl solution in cell (14). Two routes can be followed for the further elaboration:

ROUTE A :

Equation (17) is inserted into (16) to obtain:

$$p({}^{s}_{s}a_{H}) = ({}^{s}E - {}^{s}E^{o})/k - pm_{1} - {}^{s}AI^{\frac{1}{2}}/(1 + {}^{s}a_{0}\,{}^{s}BI^{\frac{1}{2}}) \qquad (18)$$

which is the ${}^{s}_{s}pH$ of the KHPh + KCl mixed solutions. The limiting value of such $p({}^{s}_{s}a_{H})$ for $I \longrightarrow I_{S}$, *i.e.* $m_{1} \longrightarrow 0$, gives the sought ${}^{s}_{s}pH_{S}$ value for KHPh (RVS) alone in the solvent s considered. The $p({}^{s}_{s}a_{H})$ *vs.* m_{1} plot is linear and the extrapolation to $m_{1} = 0$ is short and safe. An iterative calculation, requiring preliminary knowledge of the ionisation constants of *o*-phthalic acid $H_{2}Ph$, is needed to obtain I_{S} at the selected $m_{S} = 0.05$ mol/kg KHPh concentration for the total ionic strength $I = I_{S} + m_{1}$ for the equation (18).

ROUTE B :

Using the equation (17), one can write for the quantity $p({}^{s}_{s}a_{H}\ {}^{s}_{s}\gamma_{Cl})$:

$$p({}^{s}_{s}a_{H}\ {}^{s}_{s}\gamma_{Cl}) = {}^{s}_{s}pH + {}^{s}AI^{\frac{1}{2}}/(1 + {}^{s}a_{0}\,{}^{s}BI^{\frac{1}{2}}) = ({}^{s}E - {}^{s}E^{o})/k - pm_{1} \qquad (19)$$

whose limiting value for $I \longrightarrow I_{S}$ (*i.e.* for $m_{1} \longrightarrow 0$) is:

$$p({}^{s}_{s}a_{H}\ {}^{s}_{s}\gamma_{Cl})_{S} = {}^{s}_{s}pH_{S} + {}^{s}AI_{S}^{\frac{1}{2}}/(1 + {}^{s}a_{0}\,{}^{s}BI_{S}^{\frac{1}{2}}) \qquad (20)$$

wherefrom one easily obtains the required ${}^{s}_{s}pH_{S}$ value. The extrapolation to $m_{1} = 0$ from the quasi-linear $p({}^{s}_{s}a_{H}\ {}^{s}_{s}\gamma_{Cl})$ *vs.* m_{1} plot is,again,short and safe. Iterative calculations, of the same type already mentioned for Route A, are again necessary to obtain I_{S} for insertion in equation (20). Route A and Route B lead to substantially identical results for the final ${}^{s}_{s}pH_{S}$ value (refs.11,26), with uncertainties of the order of some 0.001 pH. Route B is, however, definitely preferable, for the reasons explained in paragraph 2.6 .

When the relative permittivity and other factors – *e.g.* the solvating ability – are such as to cause significant ion association, m_{1} and m_{S} must be corrected by appropriate degrees of ionisation in the mixed electrolyte, to be determined by reliable methods, and the calculation functions described above must be modified accordingly. Therefore the present treatment based on equations (17) to (22) must be intended as applicable to water-rich solvent mixtures (but also to 100%-pure nonaqueous solvents) of relative permittivities greater than about 30, due account being taken of the temperature dependence of such relative permittivities.

2.6 CONSEQUENCES OF THE pH_{S} STANDARDISATION IN AQUEOUS SOLUTION

The ion-size parameter ${}^{s}a_{0}$ in equation (17), which is generally treated as an adjustable distance of closest approach of ions for *single* binary electrolytes, was determined by various authors for a gret number of *aqueous* such electrolytes: its value ranges from 0.3 to 0.6 nm and decreases little with increasing temperature. Since in *mixed* electrolytes ${}^{s}a_{0}$ becomes much less defined and significant, for *aqueous* solutions Bates and Guggenheim suggested fixing ${}^{w}a_{0} \times {}^{w}B = 1.5\ mol^{-\frac{1}{2}}\ kg^{\frac{1}{2}}$ (which implies ${}^{w}a_{0} = 0.462$, 0.456, 0.451, 0.445, and 0.439 nm at 0, 25, 50, 75, and 100 °C, respectively) in equation (17) thus leading to the normalized expression:

$$p({}^{w}_{w}\gamma_{Cl}) = {}^{w}AI^{\frac{1}{2}}/(1 + 1.5I^{\frac{1}{2}}) \qquad (21)$$

which is known as the *Bates-Guggenheim convention* (refs.27,28) and is now internationally endorsed for pH-metric standardisation in *aqueous* solutions at $I \leq 0.1$ mol/kg. Since, obviously, there must be no break of continuity passing from pure water to, *e.g.* a solvent mixture of 99% water and 1% methanol, and the ${}^{s}B$ parameter in equation (17) is a precise and fundamental temperature-dependent physical constant, it is practical that ${}^{s}a_{0}$ in solvent mixtures with water, at each temperature, retains the same value, "normalized" in water (ref.29), by the Bates-Guggenheim convention. This link implies that, for each solvent mixture s of rela-

tive permittivity (dielectric constant) ${}^{s}\varepsilon$ and density ${}^{s}\rho$, the ${}^{s}a_0{}^{s}B$ product in equation (17) is in turn "normalized" as:

$$({}^{s}a_0{}^{s}B)_T = 1.5\ [({}^{w}\varepsilon{}^{s}\rho)/({}^{s}\varepsilon{}^{w}\rho)]^{\frac{1}{2}}_T \qquad (22)$$

at each temperature T of measurement ($^{w}\varepsilon$ and $^{w}\rho$ denote the relative permittivity and the density of pure water, respectively). [It is clear that, for the evaluation of ${}^{s}a_0$, any possible scheme alternative to that expressed by equation (22) must definitely respect the above continuity between water and water/co-solvent mixtures].

With the insertion of equation (22), equation (17) becomes the Bates-Guggenheim convention extended to solvent mixtures with water, and its validity cannot evidently be wider than for $I_S \leq 0.1$ mol/kg. In this context, Route B above offers a definite advantage over Route A (see 2.5). In fact, according to the latter, ${}^{s}E$ must be measured at $m_1 \leq (I - I_S) = (0.1/\text{mol kg}^{-1} - I_S)$, for the Bates-Guggenheim convention to be used in equation (18) to obtain the ${}^{s}_{s}\text{pH}$ values for subsequent extrapolation to $m_1 = 0$, as described above. Instead, following Route B, since the Bates-Guggenheim convention (20) operates *after* the extrapolation of $\text{p}({}^{s}_{s}a_{\text{H}}\ {}^{s}_{s}\gamma_{\text{Cl}})$ to $m_1 = 0$ gave the limiting $\text{p}({}^{s}_{s}a_{\text{H}}\ {}^{s}_{s}\gamma_{\text{Cl}})_S$ value, ${}^{s}E$ can conveniently be measured at I values well above 0.1 mol/kg, where ${}^{s}E$ may be particularly stable and reproducible, which will obviously be beneficial for the final precision of the ${}^{s}_{s}\text{pH}_S$ standard. Results obtained for the RVS in methanol/water, 1,4-dioxane/water and dimethylsulfoxide/water solvent mixtures at various temperatures are collected in Table 1.

2.7 STANDARD BUFFERS OTHER THAN POTASSIUM HYDROGENPHTHALATE

Tables 2, 3 and 4 summarize ${}^{s}_{s}\text{pH}_S$ values for standard buffer solutions, other than the selected RVS (KHPh), in some nonaqueous or mixed solvents at different temperatures. It must be pointed out that, to obtain these data, the ${}^{s}a_0$ values adopted by some author were not evaluated strictly through equations (17) and (22) (see footnotes to Tables 1 to 4). For example, in 100%-pure heavy water, dimethylsulfoxide, methanol or ethanol – at 25 °C and I = 0.01 mol kg^{-1} – taking ${}^{s}a_0$ values 25% higher than those fixed by equation (22) would make the final ${}^{s}_{s}\text{pH}_S$ values higher by 0.009, 0.019, 0.029 and 0.046 respectively, and ${}^{s}a_0$ values 50% higher would make ${}^{s}_{s}\text{pH}_S$ increase by 0.016, 0.036, 0.053 and 0.084 respectively. Therefore, when reporting newly determined ${}^{s}_{s}\text{pH}_S$ data, it is very important to specify (with appropriate definitions in the text or labellings whenever applicable – for instance: ${}^{s}a_{0[\text{BG}]}$, the bracketed initials standing for "Bates-Guggenheim convention", and so on) whether equation (22) was adopted or a different ${}^{s}a_0$ convention was selected, so as to enable the user to make the necessary corrections.

2.8 PRIMARY STANDARDS AND OPERATIONAL STANDARDS

Buffer substances other than KHPh (RVS), cf. Tables 2, 3 and 4, whose ${}^{s}_{s}\text{pH}_S$ values were assigned by the same method described for KHPh in paragraph 2.5 – namely, each buffer, mixed with various KCl concentrations in solvent s, measured in cell (14) with subsequent regression analysis of the relevant emf's ${}^{s}E$ along equations (15) to (22) – can be called *primary standards* (PS), by analogy with the official recommendations (ref.1) for aqueous solutions. Any such PS substance must meet the criteria of:

2.8.1 Preparation in a highly pure state reproducibly, and availability as certified reference material (CRM);

2.8.2 Stability of solution over a reasonable period of time;

2.8.3 Low residual liquid junction potentials foreseeable considering the junction with the salt bridge.

TABLE 1 - ${}^{s}_{s}pH_{S}$ values for the 0.05 mol/kg Potassium Hydrogenphthalate buffer solution (RVS) in various aqueous organic solvent mixtures of different wt percentage of the organic co-solvent, at various temperatures.

wt per cent of co-solvent in admixture with water	ORGANIC CO-SOLVENT								
	METHANOL (#)			1,4-DIOXANE (#)				DIMETHYLSULFOXIDE (##)	
	10 °C	25 °C	40 °C	15 °C	25 °C	35 °C	45 °C	-12 °C	+25 °C
0 (*)	3.997	4.005	4.027	3.998	4.005	4.018	4.038	-	4.005
10	4.232	4.220	4.242	4.323	4.327	4.335	4.356	-	-
20	4.483	4.460	4.472	-	-	-	-	-	4.471
30	-	-	-	5.042	5.023	5.014	5.019	4.870	4.761
50	5.162	5.129	5.127	5.784	5.789	5.792	5.790	-	-
64	5.480	5.452	5.441	-	-	-	-	-	-
84.2	6.280	6.236	6.237	-	-	-	-	-	-
Reference Nos.	13			36	14,36	36	36	12	

(*) Data in pure water from refs.1,23 .

(#) ${}^{s}a_{0} \times {}^{s}B$ product defined by equation (22).

(##) ${}^{s}a_{0} \times {}^{s}B$ taken as = 1.5 over the range of mixtures explored, causing deviations of the order of 0.001 pH with respect to equation (22).

TABLE 2 - ${}^{s}_{s}pH_{S}$ values for some buffer solutions in various water/methanol and water/ethanol solvent mixtures, at 25 °C.

wt per cent of alcohol in the mixture	WATER/METHANOL		WATER/ETHANOL			
	Buffers:		Buffers:			
	OXALATE (*)	SUCCINATE (**)	OXALATE (*)	SUCCINATE (**)	SALICYLATE (#)	DIETHYLBARBITURATE (##)
0	2.15	4.12	2.146	4.113	-	-
10	2.19	4.30	-	-	-	-
20	2.25	4.48	-	-	-	-
30	2.30	4.67	2.322	4.692	-	-
40	2.38	4.87	-	-	-	-
50	2.47	5.07	2.502	5.064	-	-
60	2.58	5.30	-	-	-	-
70	2.76	5.57	-	-	-	-
71.89	-	-	2.971	5.697	-	-
80	3.13	6.01	-	-	-	-
90	3.73	6.73	-	-	-	-
100	5.79	8.75	-	-	8.302	13.232
Reference Nos.	31 (§)		32 (§)			

(§) The extended-terms equation of Gronwall-LaMer-Sandved (ref.37) was used instead of equations (17) and (22).

(*) Oxalic acid (0.01 *m*) + LiHOxalate (0.01 *m*).

(**) Succinic acid (0.01 *m*) + LiHSuccinate (0.01 *m*).

(#) Salicylic acid (0.01 *m*) + LiSalicylate (0.01 *m*).

(##) Diethylbarbituric acid (0.01 *m*) + LiDiethylbarbiturate (0.01 *m*).

TABLE 3 - ${}^{s}_{s}pH_S$ values for some buffer solutions in different solvents, at various temperatures.

	WATER/METHANOL 50% w/w			HEAVY WATER (D_2O)		
Type of ${}^{s}_{s}pH_S$	${}^{s}_{s}pH_S$			pD_S		
	Buffers:			Buffers:		
Temperature °C	ACETATE (*)	SUCCINATE (**)	PHOSPHATE (#)	CITRATE (◇)	PHOSPHATE (##)	CARBONATE (◇◇)
5	-	-	-	4.378	7.539	10.998
10	5.518	5.720	7.937	4.352	7.504	10.924
15	5.506	5.697	7.916	4.329	7.475	10.855
20	5.498	5.680	7.898	4.310	7.449	10.793
25	5.493	5.666	7.884	4.293	7.428	10.736
30	5.493	5.656	7.872	4.279	7.411	10.685
35	5.496	5.650	7.863	4.268	7.397	10.638
40	5.502	5.648	7.858	4.260	7.387	10.597
45	-	-	-	4.253	7.381	10.560
50	-	-	-	4.250	7.377	10.527
Reference Nos.	33 (§)			34 (§)		

(§) The ${}^{s}a_0 \times {}^{s}B$ values used are in substantial agreement with equation (22).
(*) Acetic acid (0.05 *m*) + Sodium acetate (0.05 *m*) + NaCl (0.05 *m*).
(**) NaHSuccinate (0.05 *m*) + NaCl (0.05 *m*).
(#) KH_2PO_4 (0.02 *m*) + Na_2HPO_4 (0.02 *m*) + NaCl (0.02 *m*).
(##) KD_2PO_4 (0.025 *m*) + Na_2DPO_4 (0.025 *m*).
(◇) $KD_2C_6H_5O_7$ (0.05 *m*).
(◇◇) $NaDCO_3$ (0.025 *m*) + Na_2CO_3 (0.025 *m*).

TABLE 4 - ${}^{s}_{s}pH_S$ values of some buffer solutions in WATER/ETHANOL and WATER/DIMETHYLSULFOXIDE (DMSO) at various wt percentages of the organic co-solvents, at normal and subzero temperatures.

Temperature °C	CH_3COOH (0.05*m*) + CH_3COONa (0.05*m*)				KH_2PO_4 (0.025*m*) + Na_2HPO_4 (0.025*m*)				Reference Nos.
	H_2O	ETHANOL 10%	ETHANOL 20%	ETHANOL 40%	H_2O	ETHANOL 10%	ETHANOL 20%	ETHANOL 40%	
25	4.670	4.822	4.967	5.395	6.857	7.104	7.310	7.597	35 (§)
0	4.687	4.861	5.021	5.445	6.963	7.263	7.508	-	
-5	-	4.881	5.044	5.470	-	7.315	7.569	-	
-10	-	-	5.075	5.498	-	7.376	7.638	-	
	KH_2PO_4 + Na_2HPO_4 (0.008695*m*) (0.03043*m*)				KH_2PO_4 (0.025*m*) + Na_2HPO_4 (0.025*m*)				
	H_2O	DMSO 20%	DMSO 30%		H_2O	DMSO 20%	DMSO 30%		
25	7.406	7.959	8.266		6.857	7.407	7.710		12 (*)
	TES (0.070*m*) + NaTES (0.030*m*) (#)								
	H_2O	DMSO 20%	DMSO 30%						
25	7.026	7.106	7.128						
0	7.558	7.649	7.860						
-5.5	-	7.889	-						
-12	-	-	8.210						

(§) The ${}^{s}a_0 \times {}^{s}B$ values used are in substantial agreement with equation (22).
(*) ${}^{s}a_0 \times {}^{s}B$ taken as = 1.5 over the range of mixtures explored, causing deviations of the order of 0.001 pH with respect to equation (22).
(#) TES = N-tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid; NaTES = Sodium salt of TES.

However, alternatively, the assignment of the ${}^{s}_{s}pH_{S}$ values is traceable directly to the RVS, by comparing the selected buffer solution – which can be called an *operational standard* (OS) again by analogy with the official recommendation (ref.1) for aqueous solutions – with the RVS in the appropriate operational cell with liquid junction, of the type (23):

$$Pt|H_2|\text{RVS in } s||\text{Salt bridge in } s||\text{OS in } s|H_2|Pt \qquad (23)$$

where the liquid junctions are formed within vertical 1 mm capillary tubes, thus resulting in a sufficiently well defined and reproducible geometry of the junction.
In fact, from the emf E of the cell (23), assuming the cancellation of the liquid junction potentials, the ${}^{s}_{s}pH_{S}$ value of the OS is directly:

$${}^{s}_{s}pH_{OS} = {}^{s}_{s}pH_{RVS} - E/k \qquad (24)$$

Of course, each selected buffer solution can be standardised both as PS and OS, but the respective ${}^{s}_{s}pH_{PS}$ and ${}^{s}_{s}pH_{OS}$ values will be slightly different from each other due to the combined effect of the uncertainty in evaluating ${}^{s}_{s}\gamma_{Cl}$ by the convention (17) and the uncertainty in the cancellation of the liquid junction potentials in cell (23).
Any such ${}^{s}_{s}pH_{OS} - {}^{s}_{s}pH_{PS}$ difference is, however, expected to be at the level of no more than 0.02 and thus too small to be of practical significance for most ${}^{s}_{s}pH_{X}$ measurements.
Operational standards are in no way to be regarded as inferior to, but on a par with, primary standards for the purpose of ${}^{s}_{s}pH_{X}$ measurements with cell (6).

3. CERTIFIED REFERENCE MATERIALS FOR ${}^{s}_{s}pH_{S}$

National Standards Organisations and Metrological Laboratories shall be encouraged to continue to make available certified reference materials, CRM. It is desirable that criteria be established for the purity of CRM based on non-electrometric methods. Until this is possible, the CRM purity can be assessed by measurements on cell (14) or by comparison with known quality material in cell (23) or in the simpler cell (25):

$$Pt\left|H_2\right|\begin{matrix}\text{RVS, PS or OS}\\ \text{known material, in } s\end{matrix}\Big|\Big|\begin{matrix}\text{RVS, PS or OS}\\ \text{new material, in } s\end{matrix}\left|H_2\right|Pt \qquad (25)$$

where || is a sintered glass disc of appropriate porosity, and the liquid junction potential is negligible because the new RVS, PS or OS material and the known RVS, PS or OS material (obviously of the same buffer) usually will differ only very slightly in composition from each other.
Thus, from the cell emf E:

$$pH_{new} = pH_{known} - E/k \qquad (26)$$

which gives a convenient routine evaluation of the conformity of newly prepared CRM.

4. CHECKING THE INTERNAL CONSISTENCY OF ${}^{s}_{s}pH_{S}$ DATA IN HOMOLOGOUS SERIES OF MIXED SOLVENTS

Looking over the available results, both $p({}^{s}_{s}a_{H}\,{}^{s}_{s}\gamma_{Cl})_{S}$ and ${}^{s}_{s}pH_{S}$ are seen to be continuous and smooth functions of temperature and solution composition but, considering that the $p({}^{s}_{s}a_{H}\,{}^{s}_{s}\gamma_{Cl})$ values are not affected by anything extrathermodynamic – contrary to the case of ${}^{s}_{s}pH_{S}$ –, analysis of internal consistency of the $p({}^{s}_{s}a_{H}\,{}^{s}_{s}\gamma_{Cl})$ results in terms of a multilinear regression – having temperature T, mole fraction x of co-solvent and molality m_1 of KCl in cell

(14) as variables – is important. In this context a data analysis accounting for the primary medium effect variation of the thermodynamic parameters was recently set up (refs.30,13) leading to a multilinear regression equation of the type:

$$p({}^{s}_{s}a_{H}\ {}^{s}_{s}\gamma_{Cl})_{T,x} = A + Bm_1 + Cz + Dx + Exm_1 + Fzm_1 + Gz^2 + Hx^2 + Ix^3 \qquad (27)$$

where $z = (T-\theta)/\theta$ and $\theta = 298.15$ K. Data for pure water (x=0) must, of course, be included in the analysis: the constant A is evidently the value of $p({}^{s}_{s}a_{H}\ {}^{s}_{s}\gamma_{Cl})$ at $x = 0$ and 298.15 K, that is $p({}^{w}_{w}a_{H}\ {}^{w}_{w}\gamma_{Cl})_{S}$ in *water*.

This multilinear regression scheme is also important for interpolations of the final ${}^{s}_{s}pH_{S}$ data over a range of water/co-solvent mixture compositions. For example, taking the case of water/methanol, equation (28):

$${}^{s}_{s}pH_{S} = 4.00 + 4.38x - 5.02x^2 + 4.23x^3 + 0.13z - 0.91xz \quad , \qquad (28)$$

which reproduces the relevant data in Table 1 to within ±0.01, would permit appropriate interpolation of this kind of data. (However it is just to be remembered that, in spite of smoothness of correlation and accuracy of reproduction, each ${}^{s}_{s}pH_{S}$ value – either determined experimentally or interpolated through (28) – is based on its own distinct standard state at each solvent composition x studied and does, as such, *not* participate of one intersolvental scale of pH with ultimate reference to water, as equation (3) shows).

With accumulation of ${}^{s}_{s}pH_{S}$ data concerning a variety of nonaqueous solvents and/or their mixtures with water, it is clear that this type of regression equation (duly accompanied by specific information about buffer substance and ranges of solvent compositions and temperatures) becomes essential for the expected extension of pH standardisation and the interrelated metrological requirements of appropriate interpolations.

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