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PRACTICAL MEASUREMENT  
OF pH IN AMPHIPROTIC AND  
MIXED SOLVENTS

*A Report prepared by*

ROGER G. BATES

*National Bureau of Standards, Washington D.C., U.S.A.*

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**ABSTRACT**

Procedures analogous to those on which a practical pH scale has been based can be used profitably to establish operational acidity scales in certain other amphiprotic and mixed solvent media. A universal pH scale relating proton activity uniformly to the aqueous standard reference state is not yet a practical possibility, but separate scales for each medium can be achieved and will fulfil most of the requirements. The best choice of unit appears to be  $p\bar{a}_{\text{H}}^*$  or  $-\log(m_{\text{H}} \cdot s\gamma_{\text{H}})$ , where  $s\gamma_{\text{H}}$  is referred to the standard state in each particular medium  $s$ . Data for reference solutions in 50 wt. per cent methanol and in deuterium oxide are given.

**THE OPERATIONAL pH SCALE**

The well-recognized difficulty in reconciling a fundamental definition of the pH value with the practical experimental procedures for the routine measurement of acidity has led to the widespread adoption of an operational definition of the  $\text{pH}^{1-3}$

$$\text{pH}(X) - \text{pH}(S) = \frac{E_X - E_S}{(RT \ln 10)/F} \quad (1)$$

In this equation,  $X$  designates the solution of unknown pH and  $S$  the standard reference solution of known or assigned pH, while  $E$  is the electromotive force of a suitable pH cell consisting of an electrode reversible to hydrogen ions (usually a glass electrode, hydrogen gas electrode, or quinhydrone electrode) coupled with a suitable reference electrode (commonly calomel-mercury or silver-silver chloride electrode). A bridge composed of a concentrated solution of potassium chloride usually connects the reference electrode with solution  $X$  or  $S$  when the cell is filled. The symbols  $R$ ,  $T$ , and  $F$  represent the molar gas constant, the absolute temperature, and the faraday, respectively.

**INTERPRETATION OF THE MEASURED pH**

Under optimum conditions, the potential differences across the diffusion junctions  $\text{Soln. } X \mid \text{conc. KCl}$  and  $\text{Soln. } S \mid \text{conc. KCl}$  can be considered to be equal, and then the difference of e.m.f.  $E_X - E_S$  is a useful formal measure

of a relative hydrogen ion activity in the two solutions<sup>4</sup>; in other words, the left side of Eq. (1) can then be written  $p_{a_H}(X) - p_{a_H}(S)$ . To assure close equality of the junction potential, solutions  $X$  and  $S$  should match closely in pH, ionic strength, and composition, and neither should interact chemically with  $K^+$  or  $Cl^-$  ions. In particular, the pH should be neither greater than 11.5 nor less than 2.5, and the concentrations of non-electrolytes should be low and equal. Values of  $pH(S)$  for selected reference solutions correspond to a conventional hydrogen ion activity referred to the standard state for aqueous solutions:

$$pH(S) \equiv p_{a_H}(S) \quad (2)$$

This approach to pH standardization has received the endorsement of two Commissions of the International Union of Pure and Applied Chemistry<sup>5</sup>. Embracing the operational definition set forth in Eq. (1), it permits the experimental evaluation of  $pH(X)$  in a wide variety of media. Many if not most of these media differ so profoundly in composition from the standard reference solutions that the "relative hydrogen ion activity" obtained from  $pH(X) - pH(S)$  is virtually meaningless. For example, reproducible  $pH(X)$  values in nonaqueous media are often obtainable, but it is not possible to interpret these values usefully in terms of the proton level in the solution. It is the purpose of this report to recommend a procedure which, with further development, gives promise of permitting a useful interpretation, under optimum conditions, of practical pH numbers for many amphiprotic and mixed solvents. This approach, which has already been set forth elsewhere<sup>4, 6</sup>, has its roots in earlier proposals for the useful measurement of acidity in various media<sup>7-9</sup>.

### EXTENSION TO OTHER SOLVENTS

In general, the solvent should be amphiprotic, that is, be capable, like water, of either combining with protons released by acids or of furnishing protons to bases added to the medium. Furthermore, the experimental aspects of the method require that the hydrogen gas electrode and the silver-silver chloride electrode be thermodynamically reversible and stable in the medium. For the pH meter to be useful, the response of the glass electrode to hydrogen ions in the medium must also be affirmed. Solvents that meet these criteria include alcohols, alcohol-water mixtures, and deuterium oxide.

In order to establish a useful practical scale, it must be shown first that the liquid-junction potential may be reasonably constant and unaffected by a considerable variation in the acidity of the solution, as long as the solvent composition remains unchanged. A means of demonstrating this constancy has already been devised<sup>6</sup>. It is then possible to determine relative hydrogen ion activities in the medium with the hydrogen electrode [compare Eq. (1)]. It remains only to select a reference value which is consistent with the thermodynamics of the pH cell used and which will endow the measured  $pH(X)$  with a clear meaning in terms of chemical equilibria. An analogous procedure will serve for the establishment of a pD scale in deuterium oxide ( $D_2O$ ).

The data needed are (i) the e.m.f. of the pH cell with liquid junction.

$$Pt; H_2(g), \text{Soln. } X \mid \text{conc. } KCl, \text{ calomel} \quad (3)$$

where Soln.  $X$  is a buffer containing chloride ions in solvent  $s$ , (ii), the e.m.f. of the cell without liquid junction

$$\text{Pt}; \text{H}_2(g), \text{Soln. } X, \text{AgCl}; \text{Ag} \quad (4)$$

and (iii) the standard e.m.f. of cell 4 both in water ( ${}_wE^0$ ) and in solvent  $s$  ( ${}_sE^0$ ). It should be noted that a knowledge of the difference of liquid-junction potentials (or  $E_j$ , when expressed in pH units) is sufficient to make Eq. (1) exact. In other words, if  $\text{pH}(S)$  were an exact (but conventional)  $\text{p}a_{\text{H}}$  in the aqueous medium, one could write

$$\text{p}a_{\text{H}}(X) = \text{pH}(X) - E_j \quad (5)$$

where the "experimental"  $a_{\text{H}}$  would also refer to the aqueous standard state. Hereafter the designation ( $X$ ) will be omitted.

It is further noted that measurements of cell 4 can yield two acidity functions, namely  $\text{p}_w(a_{\text{H}\gamma\text{Cl}})$  and  $\text{p}_s(a_{\text{H}\gamma\text{Cl}})$  depending on whether  ${}_wE^0$  (aqueous standard state) or  ${}_sE^0$  (standard state in solvent  $s$ ) is chosen for the calculation. Similarly, molal activity coefficients are designated either  ${}_w\gamma_i$  or  ${}_s\gamma_i$ , depending on the standard state used. The difference between the two acidity functions is always

$$\text{p}_s(a_{\text{H}\gamma\text{Cl}}) - \text{p}_w(a_{\text{H}\gamma\text{Cl}}) = 2 \log m\gamma_{\text{HCl}} \quad (6)$$

where  $m\gamma_{\text{HCl}}$  is the "medium effect" for the transfer of hydrochloric acid from the aqueous standard state to the standard state in solvent  $s$ . It has been shown<sup>6</sup> that measurements of  $\text{pH}$ ,  $\text{p}_w(a_{\text{H}\gamma\text{Cl}})$ , and  $m\gamma_{\text{HCl}}$ , together with a Debye-Hückel correction for interionic effects (small for dilute buffer solutions) can lead to the useful quantity  $\delta$

$$\delta \equiv E_j - \log m\gamma_{\text{H}} \quad (7)$$

This quantity can also be derived from a comparison of "true" dissociation constants with "apparent" constants based on pH measurements<sup>10</sup>. Medium effects are characteristic only of the properties of substances in their standard states; hence, constancy of  $\delta$  when the acidity varies at a fixed solvent composition is sufficient evidence to confirm the constancy of the liquid-junction potential.<sup>6</sup>

### SELECTION OF A pH UNIT FOR AMPHIPROTIC SOLVENTS

Although some confidence in the values of  $\delta$  is justifiable, there is no way of determining  $E_j$  and  $m\gamma_{\text{H}}$  individually. Hence, a  $\text{p}a_{\text{H}}$  referred always to the aqueous standard state regardless of the solvent, though eminently desirable, does not appear possible. Considerable effort and ingenuity have been expended on various means of evaluating the medium effect for hydrogen ion<sup>11-13</sup>, but these methods have not yet reached such a degree of refinement as to warrant the establishment of a single general scale of pH. Furthermore, a barrier similar to that encountered with aqueous solutions precludes the experimental determination of hydrogen ion concentrations or  $\text{p}m_{\text{H}}^4$ .

A quantity  $\text{p}(m_{\text{H}} \cdot s\gamma_{\text{H}})$  or  $\text{p}a_{\text{H}}^*$  can, however, be derived formally from the experimental pH obtained with aqueous reference solutions, provided  $\delta$  is known, by simple difference:

$$\text{p}a_{\text{H}}^* = \text{pH}^* - \delta \quad (8)$$

The  $p_{a_H}^*$  itself has a clear meaning and is consistent with equilibrium expressions involving (as is customary) the dissociation constant  $p(sK)$ .

### OPERATIONAL pH SCALE FOR AMPHIPROTIC SOLVENTS

The use of tabulated  $\delta$  corrections to convert measured operational pH values into approximate  $p_{a_H}^*$  values thus appears to be a practical possibility. Nevertheless, a better procedure would involve the use of reference solutions prepared in a medium of the same solvent composition as the test solutions. In this way, errors attendant on the transfer of the glass electrode from the aqueous medium used for standardization to the nonaqueous test medium could be avoided. The establishment of an operational scale in each medium is thus envisioned:

$$pH^*(X) = pH^*(S) + \frac{E_X - E_S}{(RT \ln 10)/F} \quad (9)$$

### REFERENCE SOLUTIONS

As in water, the  $pH^*(S)$  of each reference solution would be identified with  $p_{a_H}^*$  determined independently for that solution. The latter is related formally to  $p_s(a_{H\gamma_{Cl}})$  by

$$p_{a_H}^* = p_s(a_{H\gamma_{Cl}}) + \log s\gamma_{Cl} \quad (10)$$

The activity coefficient  $s\gamma_{Cl}$  is predominantly a reflection of interionic forces, becoming unity at infinite dilution in the solvent  $s$ . In the absence of any physical means of evaluating single ion activities, the numerical value of  $s\gamma_{Cl}$  must depend on some convention or formula accepted for this purpose.

The formula used in aqueous solutions<sup>5</sup> makes  $\gamma_{Cl}$  in solutions of ionic strength ( $I$ ) less than 0.1 closely equal to the mean molal activity coefficient of sodium chloride at a molality of  $I$ . Furthermore, it is equivalent to assigning a value of 4.56 Å to the ion-size parameter  $\bar{a}$  in the Debye-Hückel expression

$$-\log \gamma_{Cl} = \frac{A' I^{\frac{1}{2}}}{1 + B' \bar{a} I^{\frac{1}{2}}} \quad (11)$$

To preserve consistency, a convention for  $s\gamma_{Cl}$  in other amphiprotic solvents of sufficiently high dielectric constant to avoid ion-pair formation might appropriately utilize Eq. (11) with the same value of  $\bar{a}$  selected for aqueous solutions. The values of the Debye-Hückel constants  $A'$  and  $B'$  must, of course, be modified as required by changes in the absolute temperature ( $T$ ) and the dielectric constant ( $\epsilon$ ) and density ( $d_0$ ) of the solvent concerned. Their values are given by

$$A' = \frac{1.8246 \times 10^6}{(\epsilon T)^{\frac{3}{2}}} d_0^{\frac{1}{2}} \quad (12)$$

and

$$B' = \frac{50.29}{(\epsilon T)^{\frac{1}{2}}} d_0^{\frac{1}{2}} \quad (13)$$

## ACCURACY OF PRACTICAL SCALES

By this procedure, conventional  $p_{aH}^*$  values for three series of reference solutions in 50 wt. per cent methanol-water have been determined from 10 to 40°C<sup>14</sup>. Likewise,  $p_{aD}$  values for two series of reference solutions in deuterium oxide (D<sub>2</sub>O) have been derived<sup>15</sup>. The reference values, some of which are summarized in *Table 1*, can be identified with  $pH^*(S)$  in Eq. (9) or with  $pD(S)$  in an analogous expression for  $pD$  in the solvent deuterium oxide.

*Table 1.* Conventional  $p_{aH}^*$  and  $p_{aD}$  values for reference solutions at 10, 25, and 40°C ( $m$  = molality)

Solution	$p_{aH}^*$ and $p_{aD}$ values at		
	10°C	25°C	40°C
<i>In 50 wt. per cent methanol (<math>p_{aH}^*</math>)</i>			
CH <sub>3</sub> COOH (0.05 <i>m</i> )			
CH <sub>3</sub> COONa (0.05 <i>m</i> ), NaCl (0.05 <i>m</i> )	5.52	5.49	5.50
Sodium hydrogen succinate (0.05 <i>m</i> ), NaCl (0.05 <i>m</i> )	5.72	5.67	5.65
KH <sub>2</sub> PO <sub>4</sub> (0.02 <i>m</i> ), Na <sub>2</sub> HPO <sub>4</sub> (0.02 <i>m</i> ), NaCl (0.02 <i>m</i> )	7.94	7.88	7.86
<i>In deuterium oxide (<math>p_{aD}</math>)</i>			
CH <sub>3</sub> COOD (0.05 <i>m</i> ), CH <sub>3</sub> COONa (0.05 <i>m</i> )	5.25	5.23	5.23
KD <sub>2</sub> PO <sub>4</sub> (0.025 <i>m</i> ), Na <sub>2</sub> DPO <sub>4</sub> (0.025 <i>m</i> )	7.50	7.43	7.38

The errors in  $sE^0$ , in the preparation of the solutions and materials, and in the experimental measurement of e.m.f. endow  $p_s(a_{H^+Cl})$  with an aggregate uncertainty of about 0.004 pH unit at 25°C. The uncertainty of  $pH^*$  or  $pD$  obtained from routine cell measurements by Eq. (9) will be considerably greater than this amount, however, in view of the unavoidable differences among the liquid-junction potentials when individual reference solutions and unknowns of different ionic composition are used. It is therefore unwise to expect an accuracy greater than 0.02 unit except under the most carefully controlled conditions.

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