Pure & Appl. Chem., Vol.54, No.1, pp.229-232, 1982.
Printed in Great Britain.

0033-4545/82/010229-04$03.00/0
Pergamon Press Ltd
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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

pH MEASUREMENTS IN THE MARINE ENVIRONMENT

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pH MEASUREMENTS IN THE MARINE ENVIRONMENT

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Abstract - Practical measurements of pH in the marine environment have as their usual objective the assessment of acid-base speciation. In order for accurate results to be obtained, the three pH scales in common use must be coupled each with its corresponding acid-base dissociation constant. For consistency in marine studies, it is desirable that a single procedure be selected and used by all marine scientists.

The measurement of pH occupies an important place in environmental studies and in particular in both the biological and chemical aspects of oceanography. Biological processes in the marine environment and the viability of marine organisms can be correlated usefully with the pH. Furthermore, the acid/base state of seawater bears a close relationship to the equilibrium condition of the seas as well as to the rates of chemical reactions moving toward the state of equilibrium. These processes include the exchange of carbon dioxide between atmosphere and hydrosphere and also the deposition and solution of solid carbonates. It is essential therefore that the pH be linked in a clear and exact manner to the equilibrium thermodynamics of the acid/base processes concerned.

In one of its primary applications, the pH value is an index of acid/base speciation, that is, in a simple instance, of the relative concentrations of acid and base in the conjugate system

$$\text{acid} + H_2O \rightleftharpoons \text{base} + H_3O^+ \qquad (1)$$

According to the law of mass action, the "classical" dissociation constant K_c of the acid is the proportionality constant linking the acid/base ratio (R) to the molality (m) of hydronium (hydrogen) ion , namely m_H:

$$R \equiv \frac{m_{acid}}{m_{base}} = \frac{1}{K_c} m_H \qquad (2)$$

If relative activities (a_i) are used in Eq. (2), the thermodynamic dissociation constant K replaces ^1K_c:

$$R = \frac{1}{K} \frac{\gamma_{base}}{\gamma_{acid}} a_H \qquad (3)$$

In Eq. (3), γ_{base} and γ_{acid}, the activity coefficients of the indicated species, are a function of the ionic strength.

Seawater of a fixed salinity qualifies as a "constant ionic medium" (Ref. 1 & 2); its ionic strength and the relative concentrations of the several saline constituents are nearly invariant. Under these conditions, $\gamma_{base}/\gamma_{acid}$ is also nearly constant, despite changes in the acid/base ratio. Hence,

$$R = \frac{1}{K'} a_H \qquad (4)$$

where K' has been designated the "incomplete dissociation constant".

It is thus clear that, with each definition of pH ($-\log m_H$ or $-\log a_H$) one must use the corresponding value of pK, that is, $-\log {}^{H}K_c$, $-\log K'$, or $-\log K'$, if an accurate measure of acid/base speciation is to result.

Three pH scales have found most common use in seawater; these may be distinguished by the symbols pH_{NBS}, pm_H, and pH_t. In the past, the most usual practice has been to measure pH by means of the galvanic cell with liquid junction

$$\begin{array}{l}\text{Reference}\\ \text{Electrode}\end{array} \;||\; \text{Seawater} \;|\; \begin{array}{l}H_2 \text{ Electrode or}\\ \text{Glass Electrode}\end{array} \qquad \text{(A)}$$

after standardization of the electrode assembly with the dilute buffer solutions established by the National Bureau of Standards (USA), which define a conventional activity scale of pH. As the reference solutions have ionic strengths less than 0.1 mol kg^{-1}, or about one-seventh that of seawater, a residual liquid-junction potential deprives pH_{NBS} of exact correspondence with either $-\log m_H$ (pm_H) or $-\log a_H$ (pa_H). The apparent dissociation constants determined by measurements of pH_{NBS} in seawater may be represented by K", and one has, corresponding to Eqs. (2) to (4),

$$R = \frac{1}{K''} \text{ antilog } (-pH_{NBS}) \qquad (5)$$

The uniquely favorable properties of seawater as a constant ionic medium have been shown to include stabilization of the liquid-junction potential as well as the activity coefficients (Ref. 3 & 4). Consequently, one may expect constant differences among pH_{NBS}, pm_H, and pa_H in seawater of a fixed salinity. The hydrogen ion concentration appears to be conceptually simpler and more useful than the single ion activity or the quantity antilog $(-pH_{NBS})$, which, in this instance, is not exactly defined in terms of the properties of the solution. Hence, pm_H has much to recommend it for acidity measurements in oceanography (Ref. 5).

For practical measurements of pH, it is usually found convenient to utilize cell A. Thus the nature of the pH function obtained depends on that of the standard solution with which the electrode assembly is standardized. It is possible, by use of cells without liquid junction, to determine reference values of hydrogen ion concentration (pm_H) in saline media matching natural seawater closely with respect to both composition and ionic strength (Ref. 4, 6 & 7). For this, methods paralleling those by which conventional pa_H values were assigned to the NBS buffers (Ref. 8) are suitable.

Hansson (Ref. 6) has defined a third pH unit, pH_t, for use in seawater. Also based on the emf of cells without liquid junction, pH_t represents $-\log (m_H)_t$, where $(m_H)_t$ is the sum of the molalities of free hydrogen ion and that combined (as HSO_4^-) with the sulfate present in the seawater. Thus,

$$pH_t = pm_H - \log(1+\beta_{HSO_4} m_{SO_4}) \qquad (6)$$

where β_{HSO_4} is the equilibrium constant for the formation of HSO_4^- from H^+ and SO_4^{2-}. Dissociation constants corresponding to pH_t may be designated K_t, and one has

$$R = \frac{1}{K_t} \text{ antilog } (-pH_t) \qquad (7)$$

By use of data in the literature, it is possible to express the approximate relationships among these three pH scales. In seawater of salinity 35°/oo at 25°C, m_{SO_4} is 0.029 mol kg^{-1} and β_{HSO_4} is about 12 (Ref. 7). Recent work (Ref. 4, 7, & 9) suggests that γ_H is about 0.83 and the residual liquid-junction potential correspondingly about 4.5 mV. From these values, one finds the following differences for seawater at 25°C:

$$pH_{NBS} = pa_H - 0.076 \quad (8)$$

$$pm_H = pa_H - 0.080 \quad (9)$$

and

$$pH_t = pm_H - 0.130 \quad (10)$$

When the concentrations are expressed in terms of moles per kilogram of seawater instead of moles per kilogram of water (molality), all values are increased by 0.015 unit; pH_t is then designated pH_{SWS} (Ref. 6) and pm_H becomes pM_H (Ref. 4). The differences given above remain unchanged.

It is evident from the foregoing discussion that the acid/base ratio is determined by a difference between pH and pK. For accurate results, it is essential that the pK value chosen be appropriate to the scale of pH used, namely pm_H-pK_c, pH_{NBS}-pK", or pH_t-pK_t (Ref. 10). If properly used, any of these corresponding pairs will serve equally well to assess the acid/base state of a marine system. For the maximum consistency and ease of comparison, however, it is most desirable that a single procedure be selected for universal use in marine science.

Acknowledgement - Partial support for the preparation of this report was provided by the National Science Foundation (USA) under Grant CHE76 24556.

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