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**DETERMINATION OF pH IN
HIGHLY SALINE WATERS**

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Determination of pH in highly saline waters

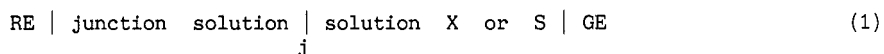
Abstract - The problem of the measurement of the operational pH in natural and artificial highly saline waters (salinity greater than in ocean water) is discussed, and tentative recommendations by which reproducible and meaningful results can be obtained are presented.

INTRODUCTION

A series of reports from this Commission has dealt with the measurement of the pH of natural waters: fresh waters (ref. 1), sea water (ref. 2), and sea water and estuarine waters (ref. 3). This report represents the conclusion of the series, dealing with highly saline waters, i.e., waters having a salt content higher than that of ocean water (a salinity of $> 35 \text{ }^0/_{00}$). Such waters can be large natural bodies of waters, such as the

Dead Sea or the Great Salt Lake, or smaller ones, such as various lagoons and sabkhas in arid zones, where evaporation often exceeds renewal, hence causing high salinities. However, the problem encompasses also artificial bodies of waters and industrial brines, such as salt pans, mining waste waters, etc. The specification of the waters dealt with in this report is, thus, that they contain a high concentration of neutral salts (mainly chlorides) and negligible concentrations of mineral acids. Knowledge of the pH of such waters is of both academic interest in the fields of geochemistry, marine chemistry and biology, and hydrology, and of practical importance for process chemistry, corrosion, and waste management.

It is a common practice to measure the pH of natural waters by means of an electrochemical cell comprising a glass electrode (GE) responsive to hydrogen ions and a reference electrode (RE) that involves a liquid junction. The emf of the cell with the test solution, $E(X)$, is compared with the emf of the cell with the same electrodes but with a standard buffer solution, $E(S)$:



The pH of the test solution is given by

$$\text{pH}(X) = \text{pH}(S) + [E(S) - E(X)]/gT - [E_j(S) - E_j(X)]/gT \quad (2)$$

where $\text{pH}(S)$ is the pH value assigned to the standard buffer employed, $g = (R/F) \ln 10$, R is the gas constant, F is the Faraday constant, and E_j is the liquid junction potential across the boundary marked by j in cell (1).

APPLICATION TO HIGHLY SALINE WATERS

The problems associated with this kind of measurement relate to the stability and reproducibility of the liquid junction, hence of the E_j values, and to the proper value of $\text{pH}(S)$ to be assigned to the standard buffer used for the calibration. Several methods have been proposed to overcome these problems, when pH is to be measured in relatively dilute salt solutions, up to and including ocean waters, but they may not be applicable to more highly saline waters.

One way to eliminate the problem of the liquid junction potential is to dispense with the liquid junction itself, and have the reference electrode immersed directly in the solu-

tions X and S (ref. 4). An Ag,AgCl reference electrode is generally specified for such measurements, and eq. (2) is then replaced with

$$\begin{aligned} \text{pH}(X) &= \text{pH}(S) + [\underline{E}(S) - \underline{E}(X)]/gT - \log [\underline{m}_{\text{Cl}}(S)/\underline{m}_{\text{Cl}}(X)] \\ &\quad - \log [\gamma_{\text{Cl}}(S)/\gamma_{\text{Cl}}(X)] \\ &= \text{pH}(S)' + [\underline{E}(S) - \underline{E}(X)]/gT - \log [\underline{m}_{\text{Cl}}(S)/\underline{m}_{\text{Cl}}(X)] \end{aligned} \quad (3)$$

The problem of the E_j values is thus transformed into a problem of the activity coefficients of the chloride ions, γ_{Cl} , which, however, is taken care of in the value of $\text{pH}(S)'$, the pH assigned to the standard buffer. This procedure seems to work well for measurements in ocean waters, where the total variability of the salinity and chlorinity (i.e., $\underline{m}_{\text{Cl}}$) is minor, and an artificial sea water standard buffer that closely matches the test ocean waters is an appropriate solution to the problem (ref. 4).

There are four drawbacks to the application of this solution to the present problem, pertaining to very divers highly saline waters. One is the appreciable solubility of silver chloride in solutions that are concentrated in chloride ions. This necessitates the saturation of the solutions with freshly precipitated silver chloride for each measurement (refs. 5, 6), since in 3 mol/L aqueous sodium chloride (3.2 molal) the solubility of AgCl is about 0.003 molal (mainly as AgCl_4^{3-} , ref. 5), and is still higher in, say, waters of the Great Salt Lake (about 4.9 molal in chloride) or the Dead Sea (about 7.2 molal). Another drawback is the danger of the poisoning of the Ag,AgCl reference electrode with bromide or sulfide ions that may be present in these saline waters. (The Dead Sea is about 0.07 molal in bromide.) Yet another drawback is the large range of salinities and chlorinities encountered in the waters that are the subject of the present report. A wide range of standard buffers would have to be prepared and assigned $\text{pH}(S)$ values, in order to match the test solutions at all closely. This is evidently impractical. A final drawback is the reluctance of workers in the field to use anything but the configuration noted in cell (1) for practical pH measurements, in contrast with what laboratory researchers may be ready to invest their time and efforts in.

Since it seems to be necessary to work with cell (1), i.e., with a cell that employs a liquid junction, efforts to minimize the problems involved in its use are required. The reproducibility of the liquid junction potentials, \underline{E}_j , can be improved by a proper design of the junction, and a J-type junction appears to be the best. The junction between the junction solution and the solution X or S is formed in the vertical capillary that is the short leg of the J-tube, with the junction solution below. A renewable junction can be formed if the junction solution can be pushed out from the J-tube by the reference electrode assembly placed in its long leg (ref. 7). This renewal also guards the inner reference electrode from contamination by components of the test solution. A constant geometry at the junction and a constant composition of the junction solution are assured in this manner, hence reproducible values of \underline{E}_j should be obtained.

The precision of the pH measurements being provided for by the proper design of the liquid junction, their accuracy can, in principle, be improved by a reduction of the absolute values of $\underline{E}_j(S)$ and $\underline{E}_j(X)$. For the common junction solution employed, 3.5 mol/L potassium chloride, used in combination with the calomel reference electrode, the value of $\underline{E}_j(X)$ with respect to the highly saline test solutions X should be very small, but it is large with respect to the dilute standard buffer solutions S (NBS buffers) recommended by IUPAC for general use in aqueous solutions having ionic strengths < 0.1 molal (ref. 8). For a calomel electrode in saturated KCl the liquid junction potential with respect to dilute aqueous buffer solutions is $\underline{E}_j = 3.2$ mV (ref. 9). The successful employment of the dilute standard buffers depends on the fact that although both $\underline{E}_j(S)$ and $\underline{E}_j(X)$ are non-negligible under these such conditions, these quantities are constant and practically equal, hence cancel out. As mentioned above, the \underline{E}_j values are not equal when X is a highly saline water and S is a dilute standard buffer. Then although constant $\underline{E}_j(S)$ and (negligible) $\underline{E}_j(X)$ can be achieved, they will not cancel out. Nor can $\underline{E}_j(S)$ be calculated to a satisfactory accuracy, even with a well defined geometry of the liquid junction, because of lack of adequate knowledge of the activity coefficients in the mixed electrolyte solutions involved.

It is expedient to rewrite eq. (2) in the following manner:

$$pH(X) = [pH(S) - E_j(S)/gT] + [E(S) - [E(X)]/gT + E_j(X)/gT] \quad (4)$$

The first term on the right hand side of eq. (4) is a constant, if the dilute NBS buffers are employed, but is unknown, whereas the last term is probably negligibly small, provided highly saline test solutions X are used. Therefore, the difference in pH between two such test solutions can be measured in such a cell:

$$pH(X_1) = pH(X_2) + [E(X_2) - E(X_1)]/gT \quad (5)$$

assuming $E_j(X_1) - E_j(X_2)$ to be effectively zero. That this is, indeed, the case can be concluded from studies that compared pH values measured in cells of type (1) with H_0 values (Hammett acidity function values) obtained by indicators, i.e., without involvement of liquid junctions (refs. 10, 11).

For example (ref. 11), a difference of 0.03 units between pH and H_0 in 7 mol/L lithium chloride containing < 1% hydrochloric acid corresponds to $|E_j(X)|$ of 1.8 mV between the calomel/conc. KCl reference electrode and the test solution. Another test solution of similar salt content but different pH would have practically the same low value of E_j , and the premise for eq. (5) is validated.

The effects of the presence of high concentrations of neutral salts in some natural bodies of water on their acidity at a given concentration of hydrogen ions is of interest. The phenomenon of increasing pH values measured on Dead Sea waters on progressive dilution with distilled water beyond the increase expected from the lower hydrogen ion concentration itself has been noted (refs. 12-14). This seems to be a real effect and not an artifact of the use of cells of type (1) for the measurements. It was explained by Krungalz (ref. 15) in terms of the salt effect on the activity coefficient of divalent anions present in the waters, specifically carbonate. On the basis of the association equilibrium constants of hydrogen ions with HCO_3^- and CO_3^{2-} , K_1 and K_2 , the relationship

$$-\log [H^+] = (1/2) \{ \log \gamma(CO_3^{2-}) + \log (K_1 + [HCO_3^-]) + 2 \log \gamma_{\pm} - \log (K_1 K_2) - \log [HCO_3^-] \} \quad (6)$$

was obtained. This simplifies to

$$pH = -\log([H^+] \gamma_{\pm}) = - (1/2) \log(K_1 K_2) + (1/2) \log \gamma(CO_3^{2-}) \quad (7)$$

if $[HCO_3^-] \gamma_{\pm}^2 \gg K_1$, as is the case with sea water (γ_{\pm} is the mean activity coefficient of H^+ and HCO_3^-). The extremely large decrease of the activity coefficient of the divalent carbonate anion with increasing salt concentrations is thus mainly responsible for the decrease of the pH from around 8.1 in Mediterranean waters to 6.0 in the depth of the Dead Sea. Again, that this is not an artifact due to the use of a reference electrode with a liquid junction was demonstrated by Ben-Yaakov and Sass (ref. 16) using measurements in a cell with an AgCl, Ag electrode without a liquid junction on artificial Dead Sea water.

It has been argued by Bates and Dickson (refs. 2, 17), among others, that a primary application of pH measurements in saline media such as sea waters is the determination of the acid/base speciation of a conjugate acid/base system:

$$[acid]/[base] = (1/K_a) [H^+] \quad (8)$$

where the square brackets may denote mol/L, mol/(kg water), or mol/(kg solution) and the acid dissociation quotient, K_a , is in the appropriate units. If the thermodynamic acid dissociation equilibrium constant, K_a^0 , is used in eq. (8), its right hand side must be multiplied by $(\gamma_{base} \gamma_H / \gamma_{acid})$ for the mol/L scale and with the appropriate other activity coefficient quotient for the other scales. In ocean water of constant salinity (say, 35⁰/₀₀) the ratio $(\gamma_{base} / \gamma_{acid})$ is approximately constant, and may be incorporated with K_a into a K_a' , and the product $a_H = [H^+] \gamma_H$ can be defined as 10^{-pH} . However, K_a will, in general, depend on the salinity, and a value determined for ocean water (of salinity 35⁰/₀₀) would not be applicable in divers highly saline waters. Thus, the definition $pH = -\log a_H = -\log [H^+] \gamma_H$ will not be generally useful. Its operational definition in

terms of cell (1) and eq. (5), with the solution X_2 identified with a suitable standard buffer, is to be preferred, as is in fact, the accepted practice.

It is still necessary to choose among the operational definitions of pH and the related standardizing buffers the one most appropriate for divers highly saline waters. The pH scales that have been used (see refs. 2, 4, 17) for ocean waters include the following.

- pH_{NBS} , using dilute aqueous buffers for standardization.

- pH_t , taking into account sulfate-bound hydrogen ions.

- pH_H , using tris in synthetic sea water for standardization.

When standardization is carried out with the dilute aqueous buffers (NBS buffers), the resulting pH_{NBS} has the disadvantage of including the residual liquid junction potential (see above), so that it corresponds to neither $-\log [H^+]$ nor $-\log a_H$ (on any of the concentration scales). This problem should be aggravated for waters that are the subject of the present report, i.e., more highly saline than ocean water, since the residual liquid junction potential would be larger.

The 'total' hydrogen ion concentration, 'free' and bound to sulfate ions as HSO_4^- , has been proposed by Hansson as the quantity to be described by the pH measurement in ocean water (ref. 4). This is because ocean water contains an appreciable concentration of sulfate, about 0.03 mol kg^{-1} . With subscript t designating total, the following relationship will be obeyed:

$$pH_t = -\log[H^+] - \log(1 + [SO_4^{2-}]/K_a(HSO_4^-)) \quad (9)$$

where $K_a(HSO_4^-)$ is about 0.08 kg mol^{-1} . However, in divers highly saline waters the sulfate concentration may be nil or any value, and such waters may contain other bases, beside sulfate, that bind hydrogen ions (fluoride, phosphate, carbonate, sulfide, borate, etc.). Furthermore, the respective K_a values will depend on the composition and ionic strength of the particular saline water studied. In such waters, therefore, this concept of 'total' hydrogen ion concentration has lost the attractiveness it may have for ocean waters.

On the other hand, standardization with a standard tris buffer (tris (hydroxymethyl) methanamine) in synthetic sea water (ref. 4) does have its merits with respect to the present problem. In a sulfate-containing (0.0293 molal) synthetic sea water of $35^{0/00}$ salinity at 25°C , the 0.04 molal equimolar tris buffer has a pH_t ($-\log \mu_{Ht}$) of 8.201 according to Ramette et al. (ref. 18). In a sulfate-free synthetic sea water of the same salinity this would correspond to 8.331, according to eq. (9) (see also ref. 2). Values at some other temperatures between 5 and 40°C were also published. The precision of the measurements was very high, mean differences between duplicates being 0.05 mV , corresponding to 0.0008 units in pH (ref. 18). The value of pH(S) assigned to the equimolar 0.04 molal tris buffer in sulfate-free synthetic sea water should therefore be reliable to better than ± 0.003 units.

Dickson (ref. 17) stated that the use of (standard) buffers based on a sea water background, having not yet found any following within the oceanographic community, would be impractical in a regime where it is impossible to match the background composition of the buffer with that of the sample (e.g., brines). Nevertheless, the considerations propounded by Khoo et al. (ref. 19) make it seem likely that standards prepared in sulfate-free synthetic (sea water) media offer a successful means of setting up a useful experimental scale for the determination of $pH = -\log \mu_H$ in saline waters.

If the pH of acidic or acidified brines is to be determined, it may be advantageous to standardize with a solution of a neutral brine of similar composition to the test solution made, say, 0.01 m in hydrochloric acid, provided this standardization brine does not contain conjugate bases of weak acids. In ignorance of the activity coefficient of the hydrochloric acid in this standardization solution, no pH value can be assigned to it, but nevertheless it has the clearly defined pH_H value of 2.00.

RECOMMENDATIONS

In view of the above discussion, it would be advantageous if agreement could be reached among the workers in the field about the following points.

1. The pH of highly saline waters should be measured with a cell of type (1), i.e., with a glass electrode responsive to hydrogen ions and a reference electrode (such as calomel) incorporating a salt bridge (3.5 mol/L KCl) that provides a liquid junction.
2. The design of the liquid junction should be so as to assure maximal reproducibilities of the measurements, e.g., with a J-type capillary and provisions for renewing the junction.
3. The cell should be calibrated with an 0.04 molal equimolar tris buffer in sulfate-free synthetic sea water of salinity $35^{0}/_{00}$ (according to Khoo et al., ref. 19). This arbitrary choice is suggested in order to provide for uniformity of practice.
4. The results of the measurements should be on the $\text{pH} = -\log m_{\text{H}}$ scale, for 'free' hydrogen ion molalities, as this is the least ambiguous quantity. The mol/(kg solution) scale may, however, be used instead of the mol/(kg water) = molality scale, if this is clearly stated and justified.
5. Experimental work should be done to confirm the assigned values of the pH of the standard tris buffer in the saline medium specified above over a wide temperature range. It should also be demonstrated experimentally that residual liquid junction potentials are indeed minimized by this choice of medium for the standard buffer with respect to any highly saline test solution.

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