

Independent estimate of the pH of Dead Sea brine

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Reprinted from LIMNOLOGY AND OCEANOGRAPHY

Vol. 22, No. 2, March 1977

Made in the United States of America

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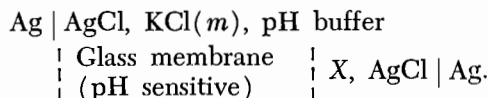
Independent estimate of the pH of Dead Sea brine

Abstract—The pH of artificial Dead Sea brine was measured by an electrochemical cell without a liquid junction. The cell consisted of a pH sensitive glass electrode and a Ag/AgCl electrode. The system was standardized in HCl solutions and pH was calculated from a measurement by this cell after estimating theoretically the activity of Cl⁻ in the brine. It is suggested that the pH of artificial Dead Sea brine is 5.86, consistent with pH values obtained by conventional pH measurements.

The pH of natural and artificial Dead Sea waters has been shown to be surprisingly low (Bodenheimer and Neev 1963; Neev and Emery 1967), ranging from 6.45 at the surface to 5.95 at depth (Nissenbaum 1969). Upon dilution with distilled water, the pH of Dead Sea water increases progressively and reaches a value of about 8.4 (Nissenbaum 1969; Amit and Bentor 1971) at the salinity of average seawater (i.e. after dilution by about 1 : 8.5). Based on a series of laboratory experiments, Nissenbaum (1969) and Amit and Bentor (1971) concluded that the carbonate system in Dead Sea water is responsible for pH variation.

The investigators cited used a conventional pH electrode pair, consisting of a pH sensitive glass membrane electrode and a reference electrode with a liquid junction (Bates 1964). At high ionic strength solutions, such as Dead Sea brines, the liquid junction potential may introduce appreciable—and unfortunately unmeasurable—error (MacInnes 1961; Bates 1964). We may ask, therefore, whether the low pH obtained through this measurement is real or is an artifact of the experimental procedure (Nissenbaum 1969). To answer this question, we have conducted a series of experiments by which the pH of Dead Sea waters could be estimated independently of liquid junction potential.

The activity of HCl in a given solution, X , can be determined electrochemically by the cell



The ideal response of this cell is represented by

$$E = E_0 - K \log(a_{\text{HCl}}), \quad (1)$$

where E = measured potential, E_0 = constant of the cell, K = slope (ideally Nernst slope $2.303 RT/F$), and a_{HCl} = activity of HCl; or

$$E = E_0 - K \log(a_{\text{H}^+} \cdot m_{\text{Cl}^-} \cdot \gamma_{\text{Cl}^-}), \quad (2)$$

where m is molality and γ activity coefficient. The pH of the tested solution can be derived from

$$\text{pH} = -\log a_{\text{H}^+} = \frac{E - E_0}{K} + \log(m_{\text{Cl}^-} \cdot \gamma_{\text{Cl}^-}). \quad (3)$$

Hence, assuming that E_0 and K are known for the cell (by calibration in standard HCl solutions), we can calculate the pH of the tested solution from these electrochemical measurements if we can determine γ_{Cl^-} in the solution independently.

A first-order estimate of γ_{Cl^-} in Dead Sea water can be obtained by first calculating $\gamma_{\pm\text{KCl}}$ in the brine through the Harned rule (Harned and Owen 1958) and then using the MacInnes convention (Garrels and Christ 1965; Garrels 1967; Lerman and Shatkay 1968), i.e.

$$\gamma_{\text{K}^+} \simeq \gamma_{\text{Cl}^-} \simeq \gamma_{\pm\text{KCl}}. \quad (4)$$

Measurements were made at $25 \pm 0.5^\circ\text{C}$ with a commercial pH electrode (Metrohm AG 9100) against a Ag/AgCl electrode (Beckman 39261). The cell was standardized in three HCl solutions 0.01 N, 0.05 N, and 0.1 N. Measurements with this cell as well as with a conventional combination pH electrode pair with liquid junction (Metrohm EA 121) were later made on artificial Dead Sea water, prepared after Amit and Bentor (1971) except that Br⁻ was replaced by Cl⁻ to prevent poisoning of the Ag/AgCl electrode (Janz 1961).

Table 1. Electrochemical measurements of standard HCl and artificial Dead Sea water.

HCl solution	pH*	EMF† (mV)	Notes
0.01 N	2.03	-156.2	From these EMF measurements K and E (Eq. 1) were evaluated to be 58.2 mV ^o and -394.4 mV
0.05 N	1.34	-233.5	
0.1 N	1.07	-266.4	
Art. Dead Sea water	6.22	-91	Artificial Dead Sea water was prepared after Amit and Bentor (1971) except that Br ⁻ was replaced by Cl ⁻

* Measured with conventional pH electrode pair with liquid junction.

† Measured with the electrochemical cell described in text.

Table 1 shows the measurements in HCl solutions and artificial Dead Sea water. The ionic concentration, in the molal scale, of the artificial Dead Sea water is given in Table 2. When Eq. 1 is applied to the HCl measurements (Table 1), E_0 and K are -394.4 mV and 58.2 mV.

The mean activity coefficient of KCl in artificial Dead Sea water was estimated by the Harned rule, which, for a multicomponent system, can be summarized in the form

$$\log \gamma_{\pm\text{KCl}} = \log \gamma_{\pm\text{KCl}(0)} + \sum \alpha_{\text{HCl}_i} I_i \quad (5)$$

where $\gamma_{\pm\text{KCl}}$ is the mean activity coefficient of KCl in the mixture; $\gamma_{\pm\text{KCl}(0)}$ is the mean activity coefficient of KCl in a pure mixture; I_i is the contribution of electrolyte i to the total ionic strength of the mixture; α_{KCl_i} is the interaction coefficient.

The activity coefficient of KCl in the absence of other electrolytes was calculated from the relationship

$$\log \gamma_{\pm\text{KCl}(0)} = \log \gamma_{\pm\text{HCl}(0)} - 0.118m_{\text{KCl}} \quad (6)$$

where m is the molality.

Equation 6 was shown to hold at high concentrations (Åkerlöf 1934, 1937; Harned and Owen 1958; Lerman 1967). Application of this relationship is necessary since data on $\gamma_{\pm\text{KCl}(0)}$ at the ionic strength of Dead Sea water are unavailable because KCl is saturated below this level.

If we apply the interaction coefficient data (α) compiled by Lerman (1967), $\gamma_{\pm\text{KCl}}$ in Dead Sea water is 0.757. The mean activity coefficient $\gamma_{\pm\text{HCl}(0)}$ required for the calculation was interpolated from the data of Harned and Owen (1958).

Inserting the measured and calculated values into Eq. 3 we obtain the estimated pH of Dead Sea water, based on the present electrochemical measurement and the assumption stated. The value thus obtained is pH 5.86, which is close to the value measured by a conventional pH electrode pair, pH 6.22 (Table 1). The difference between the two independent pH measurements is 0.36 pH units. This discrepancy is probably due to two factors: liquid junction potential error (MacInnes 1961; Bates 1964) and uncertainty in the estimation of the activity coefficient of Cl⁻ in Dead Sea water. Because of the extremely high ionic strength (8.1), it is unlikely that the discrepancy can be resolved until more de-

Table 2. Molarity and molality of artificial Dead Sea waters prepared after Amit and Bentor (1971).

Ion	Molarity* (M)	Molality (mole/kgH ₂ O)
Na ⁺	1.53	1.68
K ⁺	0.176	0.194
Ca ²⁺	0.349	0.385
Mg ²⁺	1.53	1.68
Cl ⁻	5.46	6.00
SO ₄ ²⁻	0.0083	0.0092
HCO ₃ ⁻	0.0034	0.0043
Br ⁻ †	-	-
I (ionic strength)	-	8.1

* Conversion from molarity to molality was computed through the equation molality = molarity $(\rho - G)^{-1}$ where ρ is density (measured optically to be 1.197 g/cm³) and G is total salt (kg/l) in artificial Dead Sea water.

† Br⁻ was replaced by Cl⁻.

tailed data on mixed electrolytes at high ionic strength are available.

It should be emphasized that activity coefficients of single ions and liquid junction potentials cannot be measured directly and their estimate relies on nonthermodynamic assumptions (Bates 1964). In fact, experiments similar to the one described here are the only available procedure for an experimental estimate of liquid junction potentials. If we assume that the discrepancy is due only to liquid junction potential error, we can calculate the difference between the liquid junction potential in dilute HCl solutions and in Dead Sea water to be $0.36 \times 58.5 = 21$ mV, which is not unreasonable considering the complexity and high ionic strength of Dead Sea brine.

The fact that the pH value estimated from the present measurement is lower than the directly measured value suggests that the low pH value of Dead Sea waters is probably real and is not due to experimental errors. In fact, this estimate suggests that the actual pH may be even lower than that measured with a conventional pH electrode pair. At this low pH value, about pH 6, Dead Sea waters are apparently saturated with respect to calcium carbonate (Neev and Emery 1967; Nissenbaum 1969). In contrast, if the pH of seawater is adjusted to pH 6 it will actively dissolve carbonates. It is thus clear that the behavior of the carbonate system in Dead Sea waters, and probably in other Ca-chloride brines, is markedly different from the behavior of the system in more dilute solutions. We can show (Sass and Ben-Yaakov in prep.) that this difference in behavior is directly related to the degree of ionic association of the carbonate and bicarbonate ions in the solutions under consideration.

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References

- ÅKERLÖF, C. 1934. The calculation of the composition of an aqueous solution saturated with an arbitrary number of highly soluble strong electrolytes. *J. Am. Chem. Soc.* **56**: 1439-1443.
- . 1937. A study of the composition of liquid phase in aqueous systems containing strong electrolytes of higher valence type as solid phases. *J. Phys. Chem.* **41**: 1053-1076.
- AMIT, O., AND Y. K. BENTOR. 1971. pH dilution curves of saline waters. *Chem. Geol.* **7**: 307-313.
- BATES, R. G. 1964. Determination of pH, theory and practice. Wiley.
- BODENHEIMER, W., AND D. NEEV. 1963. On the changes of pH in Dead Sea brine on dilution with distilled water. *Bull. Res. Council. Israel* **11S**: 150-151.
- GARRELS, R. M. 1967. Ion sensitive electrodes and individual ion activity coefficient, p. 344-361. In G. D. Eisenman [ed.], *Glass electrodes for hydrogen and other cations*. Dekker.
- , AND C. L. CHRIST. 1965. *Solutions, minerals and equilibria*. Harper and Row.
- HARNED, H. S., AND B. B. OWEN. 1958. *The physical chemistry of electrolyte solutions*. Reinhold.
- JANZ, G. J. 1961. Silver-silver halides electrodes, p. 179-230. In D. J. Ives and G. J. Janz [eds.], *Reference electrodes*. Academic.
- LERMAN, A. 1967. Model of chemical evolution of a chloride lake—The Dead Sea. *Geochim. Cosmochim. Acta* **31**: 2309-2330.
- , AND A. SHATKAY. 1968. Dead Sea brines: Degree of halite saturation by electrode measurements. *Earth Planet. Sci. Lett.* **5**: 63-66.
- MACINNES, D. A. 1961. *The principles of electrochemistry*, revised. Dover.
- NEEV, D., AND K. O. EMERY. 1967. The Dead Sea. Depositional processes and environment of evaporites. *Geol. Surv. Israel Bull.* **41**.
- NISSENBAUM, A. 1969. *Studies in the geochemistry of the Jordan River-Dead Sea system*. Ph.D. thesis, Univ. Calif., Los Angeles.

Submitted: 1 June 1976

Accepted: 29 September 1976