

## THE CARBONATE SYSTEM IN HYPERSALINE SOLUTIONS: DEAD SEA BRINES

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### ABSTRACT

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Various investigators reported a decrease in pH as seawater is concentrated. A similar phenomenon was reported for Dead Sea waters which are about ten times more saline than seawater. The reasons for the low pH values of Dead Sea waters (pH 5.9–6.5), which precipitate  $\text{CaCO}_3$ , were investigated by determining the apparent dissociation constants of carbonic acid in these brines. A new method, based on alkalinity titration and least-squares fitting, was used to estimate the proton activity coefficient ( $\gamma_{\text{H}^+}$ ) and the first and second dissociation constants of carbonic acid ( $K'_1$ ,  $K'_2$ ) in natural and artificial Dead Sea waters. It was found that as the salt content increases,  $\text{p}K'_1$  and  $\text{p}K'_2$  values progressively decrease whereas  $\gamma_{\text{H}^+}$  sharply increase. At the highest salinity investigated (TDS =  $330 \text{ g l}^{-1}$ )  $\gamma_{\text{H}^+}$ ,  $\text{p}K'_1$  and  $\text{p}K'_2$  values are 24.5, 5.09 and 6.23, respectively, as compared to about 0.8, 5.9, 9.1 respectively for normal seawater (19‰ chlorinity) at the same temperature (30°C).

The implication of the results of this study regarding solubility of  $\text{CaCO}_3$  and the general behavior of the carbonate system in hypersaline solutions is discussed.

### INTRODUCTION

Dead Sea waters are basically a hypersaline chloride brine (Table I), characterized by relatively high concentration of calcium and magnesium, low sodium and very low sulfate and bicarbonate concentrations.

The pH of natural and artificial Dead Sea waters has been shown to be surprisingly low (Bodenheimer and Neev, 1963; Neev and Emery, 1967; Nissenbaum, 1969; Amit and Bentor, 1971), ranging between pH 6.56 at the surface, to pH 5.95 at depth (Nissenbaum, 1969). Upon dilution with distilled water, the pH of Dead Sea waters increases progressively and reaches the value of approximately 8.4 (Nissenbaum, 1969; Amit and Bentor, 1971) at the salinity of average sea water (i.e., after a dilution factor of about 1:8.5). Based on a series of laboratory experiments, Nissenbaum (1969) and Amit

TABLE I

Chemical composition of Dead Sea waters (TDS = 289 g l<sup>-1</sup>).  
After Amit and Bentor (1971).

Ion:	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>
Molarity:	1.53	0.176	0.349	1.53	5.46	0.0083	0.0034

and Bentor (1971) concluded that the carbonate system in Dead Sea water is responsible for the pH variation. A similar trend of progressive decrease of pH with salinity was observed in the Persian Gulf by Illing et al. (1965). They reported a minimal pH value in pore water of 6.1 for chlorinity of over 150‰, and ascribed it tentatively to release of carbon dioxide due to decay of organic matter.

The low value of Dead Sea water, about pH 6, is indeed surprisingly low considering the fact that the water is close to saturation with respect to CaCO<sub>3</sub>, as is indicated by the occasional whiting and precipitation of aragonite (Neev and Emery, 1967; Nissenbaum, 1969). For comparison, if the pH of sea water is adjusted to pH 6 it will vigorously dissolve CaCO<sub>3</sub>. It would appear then that the behavior of the carbonate system in hypersaline waters is markedly different from that in sea water or fresh waters.

Aside from the general conclusion by Nissenbaum (1969) and Amit and Bentor (1971), regarding the importance of the carbonate system in controlling the pH of Dead Sea water, little is really known about the characteristics of this system in hypersaline waters. In this study we have attempted to investigate the carbonate system in Dead Sea waters using techniques and models that proved to be extremely effective in describing the system in less saline waters.

#### THEORETICAL CONSIDERATIONS

Two approaches have been extensively and successfully used to model the carbonate system in sea water: the ionic association model, and models based on apparent equilibrium constants. The association model, originally suggested by Garrels and Thompson (1962), is an extension of accepted thermodynamic conventions (Harned and Owen, 1958), by which the physico-chemical behavior of a mixed electrolyte solution is described through equilibrium constants of ionic interactions which distribute the activity of the ionic and neutral species in the solution. Although extremely useful in explaining observed phenomena (Garrels et al., 1961; Berner, 1971; Ben-Yaakov and Goldhaber, 1973), this model cannot be used, as yet, for precise calculations of ionic species due to lack of data on all relevant equilibrium constants and activity coefficients of ions in mixed electrolytes at high ionic strengths. As pointed out by Pytkowicz (1969), models based on apparent equilibrium

constants are more conveniently used in describing complex electrolytic systems due to the fact that they can readily be determined for the solution under study, and because their application does not require foreknowledge of the activity coefficients of the ion. These factors are particularly decisive in the case of hypersaline solutions for which the basic data required for the ionic speciation model are practically unknown. For these reasons it would be more practical to study the carbonate system in Dead Sea water through apparent equilibrium constants.

#### *The general pH-carbonate equations*

The basic equations necessary for quantifying the homogeneous aqueous carbonate system are (Skirrow, 1965):

$$K'_1 = \frac{a_{\text{H}^+} [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad \text{First apparent dissociation constant} \quad (1)$$

$$K'_2 = \frac{a_{\text{H}^+} [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad \text{Second apparent dissociation constant} \quad (2)$$

$$A_c = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad \text{Carbonate alkalinity} \quad (3)$$

$$C = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad \text{Total dissolved carbon (refers to inorganic carbon)} \quad (4)$$

where primes designate apparent constants, square brackets designate molar concentrations and  $a_{\text{H}^+}$  is the activity of the hydrogen (hydronium) ion.

A number of points warrant further emphasis for the sake of clarity: (a) the apparent constants so defined are unique for each relative composition as well as ionic strength, (b) the bracketed ionic concentration includes both the free and all ion pairs species save those associated with the hydrogen ion, and (c) the apparent dissociation constants  $K'_1$  and  $K'_2$  are defined relative to some arbitrary pH scale and do not require, per se, knowledge of the actual activity of the hydrogen ion in the solution. The last point is of prime practical importance due to inherent difficulty in making pH measurements in high ionic strength solutions where the error resulting from the liquid junction potential is uncertain (MacInnes, 1961; Bates, 1956, 1964).

As discussed by Ben-Yaakov (1973), the pH of an electrolytic system is controlled by the concentrations of the protolytic species (i.e., those interacting with the hydrogen ion) and total alkalinity. Total alkalinity of a solution is defined as the total (negative) charge held by all protolytic species including  $\text{H}^+$  and  $\text{OH}^-$ , which in most cases is negligibly small.

Being basically a chloride brine, the only significant protolytic species in Dead Sea water are bicarbonate and carbonate ions. Hence, eqs. 1–4 uniquely describe the pH-controlling reaction in the aqueous phase. Knowledge of the four parameters,  $K'_1$ ,  $K'_2$ ,  $A_c$  and  $C$ , is necessary and sufficient for calculating

the pH of the system and its dissolved carbonate species.

By simple algebraic manipulation of eqs. 1–4, one obtains the following expression:

$$\frac{A_c}{C} = \frac{K'_1 a_{H^+} + 2K'_1 K'_2}{(a_{H^+})^2 + K'_1 a_{H^+} + K'_1 K'_2} \quad (5)$$

It is evident from this equation that if  $K'_1$  and  $K'_2$  are kept constant, a specific  $A_c/C$  ratio defines a unique  $a_{H^+}$  (or pH), and an increase of  $A_c/C$  is associated with a decrease of  $a_{H^+}$  (or increase of pH).

Neglecting possible escape of  $CO_2$ , dilution of Dead Sea brine with distilled water should not change the ratio  $A_c/C$ . Hence, variation of pH upon dilution of Dead Sea brine (Nissenbaum, 1969; Amit and Bentor, 1971), implies that  $K'_1$  and  $K'_2$  variations must be responsible for the observed phenomenon. Natural evaporation of brines is, of course, not necessarily the inverse of dilution with distilled water. Interaction with the solid phase and with the atmosphere could change  $A_c$  or  $C$  independently and hence affect the pH. However, the similarity in trend of pH variation between natural brines and monitored laboratory solutions seems to be related to the same effect, namely change in apparent dissociation constants.

## DATA COLLECTION AND EXPERIMENTAL

### *Samples*

Natural samples were collected in the northern, deep basin of the Dead Sea. One sample was taken from a depth of 1 m, the other from a depth of 50 m. Three synthetic Dead Sea waters (DSW) were prepared using the recipe of Amit and Bentor (1971). One of the samples was prepared with no sulfate. No special effort was made in order to duplicate exact total dissolved solid (TDS), alkalinity and total dissolved carbon. The natural and synthetic solutions were diluted by a factor of two, and one of them by a factor of ten. In all, eleven solutions were studied.

### *Determination of TDS*

The operational determinations of TDS and density of the studied samples were carried out by the use of a refractometer. The functional relationship between the refractive index ( $n$ ), TDS and density was determined on a set of six solutions with known TDS, covering the range 0–289 g l<sup>-1</sup>. A synthetic solution was prepared according to Amit and Bentor (1971) and diluted to the desired TDS with distilled water.

The refractive index was measured by a thermostatically controlled Zeiss Abbe refractometer model A. In these measurements, the fourth decimal is estimated. This corresponds to a ±0.5% error in TDS determination, which

was considered adequate for the present study. The advantage of the refractive index method being the short time (a few minutes) and small amount of sample (a few drops) needed for each measurement.

The density,  $d$ , was determined by a 25-ml pycnometer calibrated with distilled water. Density results are expressed in  $\sigma$  values, where  $\sigma \equiv (d - 1)1000$ .

The following empirical equations express the relations between these parameters at 30°C:

$$\text{TDS} = (1.2401 - 2.3262n + 1.0475n^2) \cdot 10^4 \quad (\text{Fig. 1}) \quad (8)$$

$$\text{TDS} = 5.968 + 1.313\sigma + 5.995 \cdot 10^{-4} \sigma^2 \quad (9)$$

$$\sigma = -4875.1805 + 3655.9859n \quad (10)$$

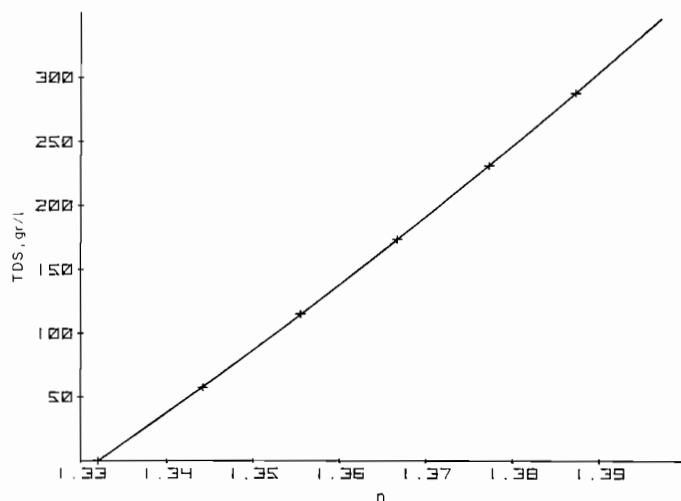


Fig. 1. Relationship between Total Dissolved Solids (TDS) and refractive index ( $n$ ) for synthetic Dead Sea brine ( $289 \text{ g l}^{-1}$ ) and diluted samples.

#### *HCl titration*

50 ml samples were titrated with 1 N HCl. Titration was carried out in a covered water-jacket vessel (Metrohm model EA 880 t-20), thermostatically controlled to  $30 \pm 0.1^\circ\text{C}$ . The acid was delivered through an immersed capillary tip of a micrometer burette (Aglar), accurate to 0.001 ml. The pH of the titrated solution was monitored with a Metrohm combined electrode (EA 121) connected to a Radiometer pH meter (model PHM-22) and scale expander model PHA-630. The pH set-up was calibrated with pH 4 and pH 7 buffers (BDH).

#### *NaHCO<sub>3</sub> titration*

Natural and diluted DSW samples (50 ml) were titrated with 0.5 N NaHCO<sub>3</sub>

solution. The titration was carried out in a closed water-jacket vessel thermostatically controlled to  $30 \pm 0.1^\circ\text{C}$ .

#### EXPERIMENTAL RESULTS

Table II contains the basic data of the studied solutions, as well as some experimental critical values and calculated results.

A typical HCl titration of Dead Sea brine is depicted in Fig. 2, and com-

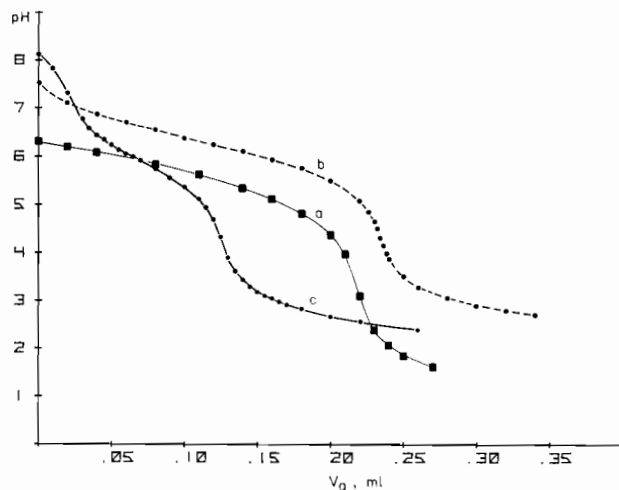


Fig. 2. Typical HCl titrations: a, Dead Sea brine (sample 2); b, fresh water; c, seawater (41‰ salinity, Gulf of Elat). Initial volume is 50 ml. Acid concentration 1 N.

pared to HCl titrations of fresh water and seawater (Gulf of Elat, 41‰ salinity). Two typical  $\text{NaHCO}_3$  titration curves are given in Fig. 3.

The following observations can be made from the original experimental data:

(1) The pH of the samples (initial pH,  $\text{pH}_i$ , Table II) decreases with increased TDS. This agrees well with the data reported by Neev and Emery (1967), Nissenbaum (1969), Amit and Bentor (1971), and also with the data reported by Illing et al. (1965) for the Persian Gulf.

(2) The pH at the inflection of the HCl titration is also a function of TDS. The "equivalence pH" ( $\text{pH}_e$ , Table II) decreases with an increase in TDS.

(3) Judging from the titration curves (Fig. 2), the behavior of Dead Sea brines resembles, paradoxically, that of fresh water. This resemblance is due to the fact that in both cases only one point of minimum buffer capacity is observed as compared to two such points in seawater. As discussed below, this resemblance is superficial as two entirely different mechanisms are involved.

(4) All  $\text{NaHCO}_3$  titrations for natural and diluted DSW result in a drop in pH (Fig. 3). This particular behavior cannot be predicted a priori and it has

TABLE II

Data and parameters of natural and synthetic Dead Sea brines

Source	Sample No.										
	1	2	3	4	5	6	7	8	9	10	11
Dilution	1	0.5	1	0.5	1	0.5	0.1	1	0.5	1	0.5
TDS (g l <sup>-1</sup> )	309	155	330	166	284	142	28	287	144	283	141
$\sigma$	210	109	223	116	194	100		196	101	193	99
Initial pH											
	pH <sub>i</sub> (measured)	6.46	7.42	6.32	7.33	6.14	7.77	6.14	6.96	6.15	7.08
	pH <sub>i</sub> <sup>*</sup> (calculated)	6.82	7.89	6.66	7.84	6.14	7.74	6.14	6.98	6.16	7.08
Equivalence pH											
	pHe (inflection)	3.35	4.29	3.25	4.13	3.43	4.93	3.26	4.04	3.31	4.03
	pHe (calculated)	3.27	4.12	3.14	4.05	3.36	4.82	3.21	3.96	3.24	3.98
First regression											
	A · 10 <sup>3</sup>	4.401	2.194	4.442	2.222	2.688	0.261	3.863	1.923	3.380	1.670
	$\gamma$ H <sup>+</sup>	17.8	2.99	24.5	3.66	13.4	0.92	14.1	2.72	13.9	2.74
	r	0.9999	1.0000	0.9997	1.0000	0.9997	1.0000	0.9999	1.0000	0.9996	1.0000
Second regression											
	total C · 10 <sup>3</sup>	2.53	1.21	2.59	1.22	1.79	0.22	2.77	1.62	2.15	1.33
	pK <sub>1</sub>	5.19	5.80	5.09	5.74	5.09	5.95	5.01	5.57	4.96	5.53
	pK <sub>2</sub>	6.34	7.24	6.23	7.15	6.03	8.39	6.23	7.52	5.96	7.48
	r	-0.9087	-0.9203	-0.9277	-0.9010	-0.9982	-0.9911	-1.0000	-0.9995	-0.9993	-0.9994
	pK <sub>12</sub>	5.76	6.52	5.66	6.44	5.56	7.17	5.62	6.54	5.46	6.50
	pH <sub>12</sub>	5.82	6.57	5.70	6.54						

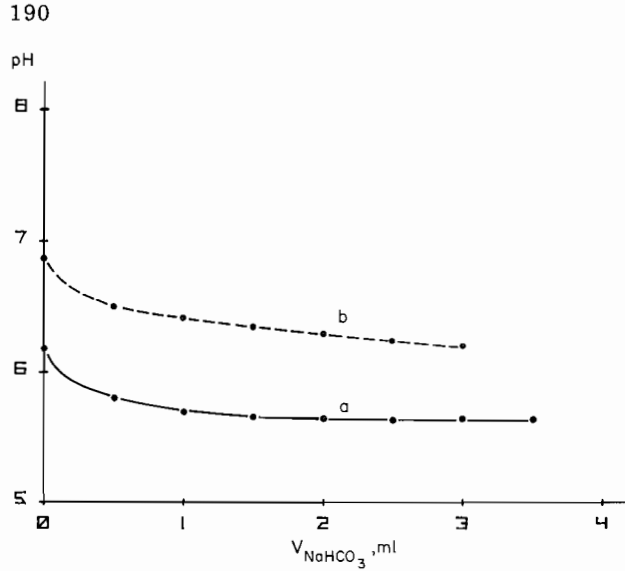


Fig. 3. Representative  $\text{NaHCO}_3$  titration. a, Dead Sea brine (sample 2); b, 0.5 dilution of above (sample 3). Initial volume is 50 ml.  $\text{NaHCO}_3$  concentration 0.5 N.

an important bearing upon our interpretation of the system. The final pH values of these titrations ( $\text{pH}_{12}^*$ ) are given in Table II.

#### MODEL CALCULATIONS

##### *HCl titration: general equation*

During HCl titration, carbonate alkalinity (eq.3) no longer describes the requirement of charge balance. Also, original alkalinity and total dissolved carbon (inorganic) decrease due to dilution.

By taking into account dilution effect, the addition of acid, and concentration of hydrogen ion (but neglecting  $[\text{OH}^-]$ ), the constraint of electrical neutrality is expressed as:

$$A \frac{V_o}{V_o + V_a} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] + N_a \frac{V_a}{V_o + V_a} \quad (11)$$

where

$V_o$  = initial volume of sample,  
 $V_a$  = volume of added HCl solution,  
 $N_a$  = normality of titration HCl solution.

In a similar way, the constraint of mass balance conservation of total dissolved carbon becomes:

$$C \frac{V_o}{V_o + V_a} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (12)$$



Combining eqs. 11, 12, 1 and 2, and using the relationship  $[H^+] = a_{H^+}/\gamma_{H^+}$ , the general titration equation is obtained:

$$\frac{1}{V_o} \left[ AV_o + \frac{a_{H^+}}{\gamma_{H^+}} (V_o + V_a) - N_a V_a \right] = C \frac{K'_1 a_{H^+} + 2K'_1 K'_2}{(a_{H^+})^2 + K'_1 a_{H^+} + K'_1 K'_2} \quad (13)$$

*Determination of A and  $\gamma_{H^+}$*

At low pH, beyond the equivalence point, most of the dissolved carbon is converted into neutral  $H_2CO_3$ , and the contribution of charged carbon species to electrical balance becomes negligibly small. The right-hand term of equation (13) can therefore be neglected to yield the equation:

$$a_{H^+} \cdot (V_o + V_a) = -AV_o\gamma_{H^+} + N_a \gamma_{H^+} \cdot V_a \quad (14)$$

This equation can be represented as a linear relationship of the form:

$$y = m + kx \quad (15)$$

where

$$y = a_{H^+} \cdot (V_o + V_a)$$

$$x = V_a$$

$$m = -AV_o\gamma_{H^+}$$

$$k = N_a\gamma_{H^+}$$

Using linear regression  $m$  and  $k$  in (15) can be estimated and used to derive  $\gamma_{H^+}$  and A.

This calculation was carried out on titration points at pH values at least 0.8 pH units below the inflection point.

*Determination of  $pK'_1$  and  $pK'_2$*

By defining  $Z$  as the left-hand term of equation (13) and rearranging the equation, one obtains:

$$\frac{Z(a_{H^+})^2}{2K'_2 + a_{H^+}} = CK'_1 - K'_1 Z \frac{K'_2 + a_{H^+}}{2K'_2 + a_{H^+}} \quad (16)$$

Once A and  $\gamma_{H^+}$  have been determined from eq.14,  $Z$  becomes a known variable, and hence eq.16 includes three unknowns: C,  $K'_1$  and  $K'_2$ . By guessing  $K'_2$ , eq.16 takes the linear form of eq.15, where

$$y = \frac{Z(a_{H^+})^2}{2K'_2 + a_{H^+}}$$

$$x = Z \frac{K'_2 + a_{H^+}}{2K'_2 + a_{H^+}}$$

$$m = CK'_1$$

$$k = -K'_1$$

Using linear regression  $C$ ,  $K'_1$  and  $r^2$  (coefficient of determination) are obtained.  $r^2$  serves as an indicator as to how good is the guessed value of  $K'_2$ . The calculation is repeated for successive estimates of  $K'_2$  until  $r^2$  is closest to 1. The calculated  $K'_1$  and  $C$  at that particular  $K'_2$  thus provide the best fit of the titration points to the model. This numerical procedure is presented graphically in Fig. 4.

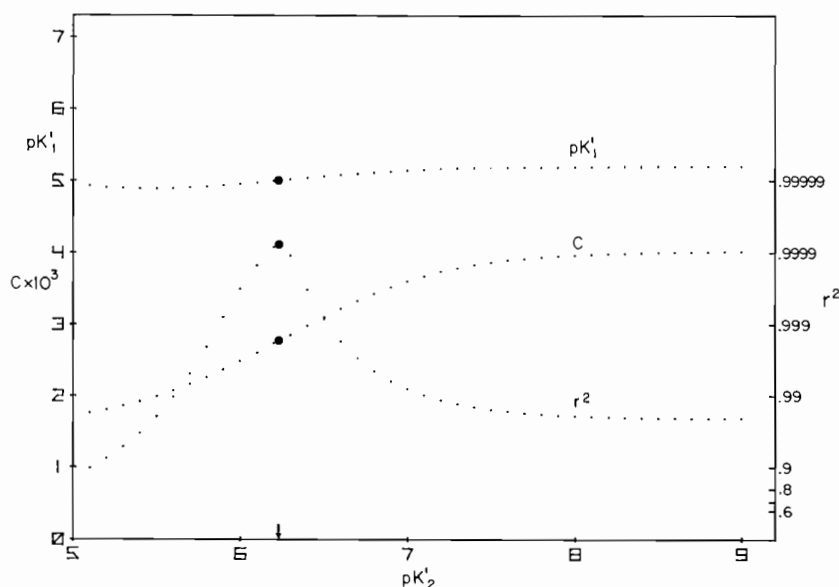


Fig. 4. A graphic demonstration of the iteration process for finding  $pK'_1$ ,  $pK'_2$  and total dissolved carbon ( $C$ ) in sample 8. Each assumed  $pK'_2$  is associated with definite calculated  $pK'_1$ ,  $C$  and  $r^2$  (coefficient of determination). Best fit is achieved where  $r^2$  is maximal. The actual values found for the maximal  $r^2$  (0.99992) are:  $pK'_2 = 6.23$ ,  $pK'_1 = 5.01$ ,  $C = 2.77 \cdot 10^{-3}$ . (Note: the scale for  $r^2$  is constructed as  $-\log(1 - r^2)$ , to allow expansion of small differences in  $r^2$  values close to 1.)

The calculation was carried out on titration points whose pH values are at least 0.5 unit above the equivalence pH.

It should be pointed out that the methods used by other investigators to analyze acid titration of seawater (Dyrssen and Sillén, 1967; Edmond, 1970) cannot be applied to Dead Sea brines. This is due to the approximate nature of the previous analyses, an approximation which is justified for seawater but cannot be applied here. In this approximate analysis, the second dissociation of carbonic acid is neglected because the pH along the titration curve is much smaller than  $pK'_2$ . As will be shown later, this assumption does not hold for acid titration of DSW.

### HCl titration results

The calculated results of alkalinity, total dissolved carbon,  $\gamma_{H^+}$ ,  $pK'_1$ ,  $pK'_2$  and their respective correlation coefficients ( $r$ ) are given in Table II. Fig. 5 describes the dependence of  $\gamma_{H^+}$  upon TDS. Fig. 6 presents the relationship between calculated  $pK'_1$ ,  $pK'_2$  and TDS.

The following empirical equations describe the relationships between the intensive parameters and TDS at 30°C:

$$\log \gamma_{H^+} = -0.14182 + 0.00360 \text{ TDS} + 3.120 \cdot 10^{-6} \text{ TDS}^2$$

$$pK'_1 = 6.1568 - 0.00352 \text{ TDS}$$

$$pK'_2 = 8.5503 - 0.0080 \text{ TDS}$$

### NaHCO<sub>3</sub> titration

An independent check on the  $pK'_1$  and  $pK'_2$  values, calculated by the procedure described above, was obtained by the NaHCO<sub>3</sub> titration. Following Deffeyes (1965), the interdependence of carbonate alkalinity, total dissolved carbon and pH can be presented schematically by an A<sub>c</sub>-C diagram (Fig. 7). The diagram is derived from eq.5 and contains straight pH locus lines for fixed A<sub>c</sub>/C. When this ratio is equal to unity, eq.5 reduces to:

$$(a_{H^+})^2 = K'_1 K'_2 \quad (17)$$

or:

$$pH_{12} = 0.5(pK'_1 + pK'_2) \quad (18)$$

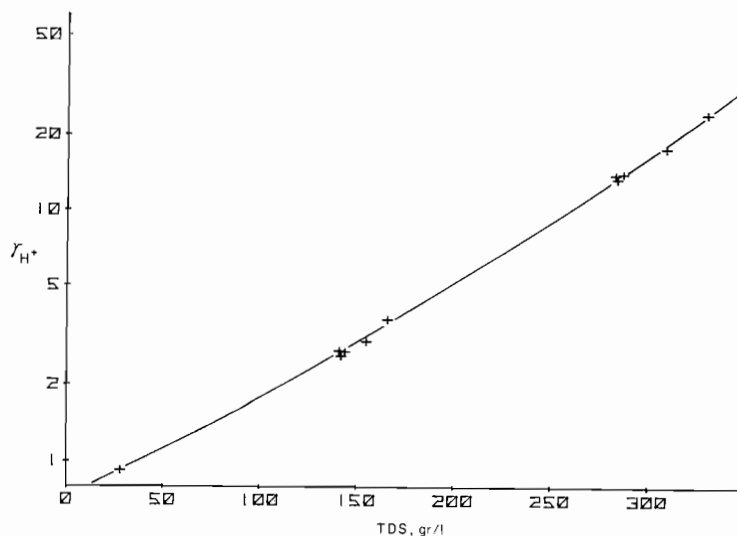


Fig. 5. Dependence of  $\log \gamma_{H^+}$  upon TDS of Dead Sea brines and their dilutions, as determined in this study.

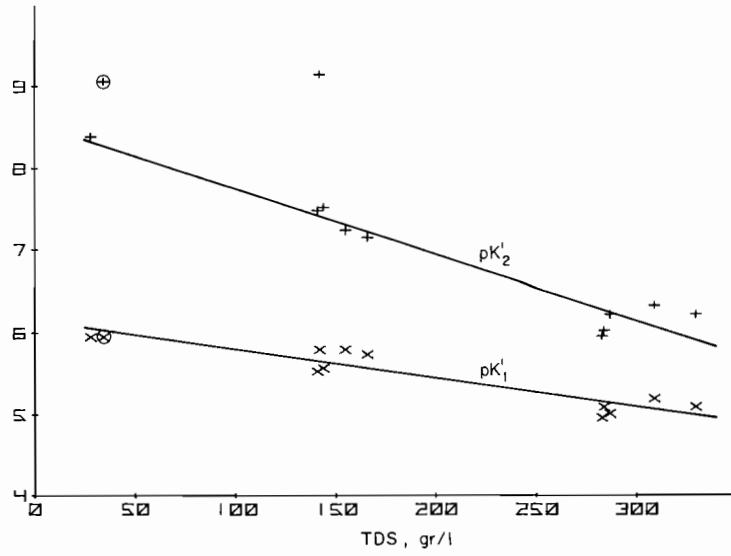


Fig. 6. Dependence of  $pK'_1$  and  $pK'_2$  on TDS for original and diluted Dead Sea brines. Sea-water values (encircled) are included for comparison.

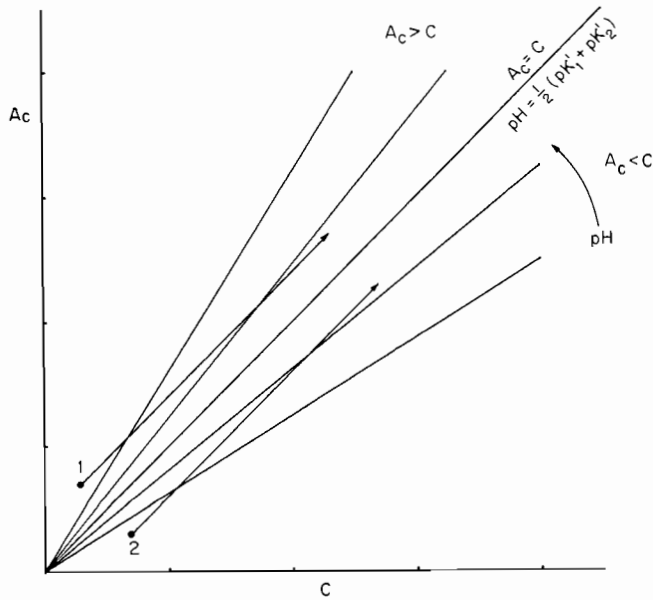


Fig. 7. Carbonate alkalinity—total dissolved carbon diagram, showing schematically lines of equal pH values. This diagram is divided by a line along which  $A_c = C$ , where the pH equals the mean of  $pK'_1$  and  $pK'_2$  ( $pH_{12}$ ). Arrows 1 and 2 represent titration paths with  $NaHCO_3$  ( $\Delta A = \Delta C$ ), and show how pH decreases or increases respectively, depending on the initial  $A_c/C$  ratio.

That is,  $\text{pH}_{12}$  equals the mean of  $\text{pK}'_1$  and  $\text{pK}'_2$  which we defined as  $\text{pK}'_{12}$ . During  $\text{NaHCO}_3$  titration ( $\Delta A = \Delta C$ ), pH will decrease if  $A > C$  and increase if  $A < C$ . For both cases, addition of  $\text{NaHCO}_3$  will cause the pH to approach the limiting value of  $\text{pH}_{12}$  (Weyl, 1961). The final pH values are thus close to but not identical with  $\text{pH}_{12}$ , and are designated therefore as  $\text{pH}_{12}^*$  (Table II).

The distinct drop in pH during  $\text{NaHCO}_3$  titration of DSW (Table II and Fig. 3) leads to the conclusion that  $A > C$  and excludes the possibility of high  $\text{P}_{\text{CO}_2}$  as an explanation for the low initial pH values of DSW.

## DISCUSSION

A basic question to be asked in view of the low pH values of Dead Sea water (and other calcium-chloride brines) is whether these values are real ones, or whether they represent a measurement artifact due to liquid junction error (Bates, 1964). The subject was studied by measurements with an Ag/AgCl reference electrode without liquid junction. Details and results are reported elsewhere (Ben-Yaakov and Sass, 1977). The pH value thus measured is similar to the values obtained by the conventional pH electrode pair. It suggests, therefore, that the measured pH values of Dead Sea water are good approximations of hydrogen ion activity.

The results for  $C$ ,  $\text{pK}'_1$  and  $\text{pK}'_2$  are not as satisfactory as the ones for  $A$  and  $\gamma_{\text{H}^+}$ . Of the eleven samples analyzed, one of the results for  $\text{pK}'_2$  (sample 6; Table II and Fig. 6) is clearly erroneous. But even after excluding this sample, regression analysis of the various parameters against TDS yields  $r^2$  for  $\log \gamma_{\text{H}^+}$  (0.9992) which is significantly higher than those for  $\text{pK}'_1$  (0.8479) and  $\text{pK}'_2$  (0.9377). Also, whereas alkalinity values of diluted samples are proportional to their TDS, deviations from proportionality are found for total carbon (Table II).

Another test for internal consistency is achieved by recalculating desired pH value of a synthetic titration curve (by solving eq.13 for  $a_{\text{H}^+}$ ) and comparing it with the experimental titration curve. Using this approach it was found that calculated initial pH values ( $\text{pH}_i^*$ ) for natural DSW, exceeded the measured one ( $\text{pHi}$ ) by as much as 0.5 unit (Table II).

This discrepancy is explained by considering the experimental set-up which allowed slight escape of  $\text{CO}_2$  during titration, and resulted in non-equilibrium pH values. Consequently, the conditions for linearity of eq.16 are not closely observed, and some error in  $\text{pK}'_1$ ,  $\text{pK}'_2$  and  $C$  is obtained. This is expressed also in absolute  $r$  (correlation coefficient) as low as 0.901, compared with values exceeding 0.999 for the alkalinity and  $\gamma_{\text{H}^+}$  regression (Table II). The correlation coefficients are poorer for natural DSW which is higher in alkalinity and total carbon than the corresponding synthetic solutions. Higher  $\text{P}_{\text{CO}_2}$  is thus built up during titration and larger amounts of  $\text{CO}_2$  escape.

However, two tests seem to suggest that the experimental errors are not so large as to significantly bias the general conclusions drawn from the data:

- (a) As discussed above, the final pH values of the  $\text{NaHCO}_3$  titration ( $\text{pH}_{12}^*$ )

represent an upper limit to  $pK'_{12}$  value. The  $pK'_{12}$  calculated from the acid titration are indeed lower by 0.04–0.1 from  $pH^*_2$  (Table II). Hence, these two independent determinations seem to support each other.

(b) The inflection point pH of the acid titration curve ( $pH_e$ ) for Dead Sea brines (samples 1 and 3, Table II) is about 3.3, significantly lower than that of seawater ( $\sim 4.5$ ). The reasons for this difference are visualized as follows: The equivalence point is defined for the condition  $AV_o = N_aV_a$ . At this point the values of  $K'_1$  and  $K'_2$  are much smaller than  $a_{H^+}$ , and eq.13 can be simplified to the form:

$$(a_{H^+})^2 = CK'_1\gamma_{H^+} \frac{V_o}{V_o + V_a} \quad (19)$$

or:

$$pH_e = 0.5 \left[ pK'_1 - \log C - \log \gamma_{H^+} - \log \frac{V_o}{V_o + V_a} \right] \quad (20)$$

Of the various terms appearing in eq.20, the last one is close to zero, since  $V_a$  is much smaller than  $V_o$ . The pH at the equivalence point is therefore mainly controlled by  $K'_1$ ,  $C$  and  $\gamma_{H^+}$ . In Dead Sea brine,  $C$  concentration ( $\sim 2.5 \cdot 10^{-3}$ ) is not markedly different from that of seawater, and cannot be the reason for the low  $pH_e$ . Remaining therefore are the high  $K'_1$  and  $\gamma_{H^+}$  values in explaining the relatively low  $pH_e$  values relative to that of seawater.

The pH at the equivalence point ( $pH_e^*$ ), calculated by eq.20, compares well with the experimentally determined one ( $pH_e$ , Table II), thus supporting the calculated values of  $pK'_1$ ,  $\gamma_{H^+}$  and  $C$ .

The present study suggests that  $K'_1$ ,  $K'_2$  and  $\gamma_{H^+}$  values in Dead Sea brines are considerably larger than ever reported for any natural waters. The data suggest that  $K'_1$  in Dead Sea waters is about ten times larger than its value in seawater,  $K'_2$  about a thousandfold larger than in seawater (Lyman, 1957; Edmond and Gieskes, 1970) and  $\gamma_{H^+}$  is about thirty times larger than the value estimated for seawater (Leyendekkers, 1973). However, the trend in  $K'_1$ ,  $K'_2$  and  $\gamma_{H^+}$  values, i.e., increase when salt concentration increases, follows the trend in seawater.

The relatively high values of  $\gamma_{H^+}$  estimated here (Fig.5 and Table II), are also in accordance with recent studies on single ion activities. The activity coefficient of the hydrogen ion in a multicomponent system, such as Dead Sea waters could be estimated by considering the activity coefficient of  $H^+$  in pure HCl solution and by taking into account interaction with other salts present (Leyendekkers, 1973). Since most of the interaction constants are unknown for Dead Sea waters, this procedure cannot be carried out numerically. However, it is expected that such a calculation would result in a high value for  $\gamma_{H^+}$  because the activity coefficient of the hydrogen ion in highly concentrated hydrochloric acid should be high. This has been attributed to the relatively high (8) hydration number of HCl (Bates et al., 1970).

Ben-Yaakov and Goldhaber (1973) defined and estimated for seawater sensitivity parameters ( $S_{K'}^i$ ) for the apparent constants of the carbonate system with respect to the major ions in the solution:

$$S_{K'}^i \equiv \frac{\Delta K'/K'}{\Delta n_i/n_i}$$

where  $K'$  is an apparent constant,  $n_i$  the concentration of an ion  $i$ . It was shown that the apparent constants are highly sensitive to a variation in the concentration of magnesium in solution. It was further shown that  $K'_2$  is about threefold more sensitive to variation in magnesium concentration than is  $K'_1$ . It should be attributed to relatively high stability of the  $\text{MgCO}_3^0$  complex as compared to that of  $\text{MgHCO}_3^-$  (Garrels and Thompson, 1962). Hence, as magnesium concentration increases a larger proportion of  $\text{CO}_3^{2-}$  relative to  $\text{HCO}_3^-$  is complexed, which has the net effect of increasing  $K'_2$  more than  $K'_1$ . This same effect, although to a smaller extent, holds for the sensitivity parameters of  $K'_1$  and  $K'_2$  with respect to sodium and potassium.

This argument is strengthened in view of the chemical composition of Dead Sea waters (Table I). It is seen that relative to Cl, and compared with seawater, Mg and Ca are enriched by a factor of about three, whereas Na is depleted by the same factor.

The important role of magnesium in affecting the pH by ion pairing was stressed also by Wangersky (1972). Another contributing factor is the negligible concentration of  $\text{SO}_4^{2-}$  in DSW (Table I). Following Wangersky (1972), sulfate ions compete with carbonate in ion pairing with magnesium. Decrease of sulfate allows more carbonate to be tied up with magnesium, thus contributing to the decrease of pH.

The interaction between major ions and the bicarbonate and carbonate ions are responsible for the increase in  $K'_1$  and  $K'_2$  as salt concentration is increased. As discussed above, the increase in  $K'_2$  is steeper than that of  $K'_1$  and the difference between the two apparent constants becomes smaller as salt concentration is increased. The difference between  $\text{p}K'_2$  and  $\text{p}K'_1$  in distilled water is 3.96, for seawater of 19% chlorinity 3.04, and for Dead Sea waters 1.14.

The marked increase in carbonate ion complexing should also increase the apparent solubility constant  $K'_{\text{sp}}$  of  $\text{CaCO}_3$  in Dead Sea brines (Garrels et al., 1969). This constant is defined in terms of total concentration, i.e., the product of  $\text{CO}_3^{2-}$  (total) and  $\text{Ca}^{2+}$  (total). Assuming that Dead Sea brines are saturated with respect to aragonite (which is precipitating occasionally from the water) one can calculate the apparent solubility product of aragonite for surface Dead Sea brine (sample 1) as follows:

Based on Neev and Emery's (1967) data,  $[\text{Ca}^{2+}]$  for TDS of  $309 \text{ g l}^{-1}$  (Dead Sea surface water, sample 1) is  $4.21 \cdot 10^{-1}$ .

$[\text{CO}_3^{2-}]$  is obtained from the relationship:

$$[\text{CO}_3^{2-}] = A_c K'_2 / (a_{\text{H}^+} + 2K'_2)$$

Using the data of Table II, one obtains a value of  $6.7 \cdot 10^{-4}$  for  $K'_{sp}$  at  $30^{\circ}\text{C}$ , which is about a thousandfold larger than the corresponding value for seawater (Edmond and Gieskes, 1970; Ben-Yaakov and Goldhaber, 1973). In a similar way, the solubility of  $\text{CaCO}_3$  in seawater is more than a hundredfold larger than the solubility in distilled water (Ben-Yaakov and Goldhaber, 1973).

The foregoing discussions suggest that the chemistry of the carbonate system in Dead Sea brines differ in degree of interaction and not in nature from the carbonate chemistry in less saline waters. An increase in brine salinity should result, in general, in a decrease in pH and an increase in  $\text{CaCO}_3$  solubility. Hence, low pH values of brines does not imply, by itself, a total  $\text{CO}_2$  increase, as tentatively assumed by Illing et al. (1965) for resolving their observation of low pH values of Persian Gulf brines.

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