Boiling Point Elevations of Sea Water and Its Concentrates

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Literature data on vapor pressures of sea water solutions and its concentrates were evaluated using the rule of additivity of molar vapor pressure depressions. A table of selected boiling point elevation data is presented in the 20° to 180° C. range for sea water and its concentrates up to threefold concentration.

EXACT DATA on the boiling points of sea water and its concentrates are needed to design desalination installations. Very precise data are required because as much as 20 or more stages are sometimes connected into series, and a small error in the boiling point of each stage could lead to substantial differences in the end results. Furthermore, the vapor pressure of a solution is very sensitive to temperature. At the present time the data of Stoughton and Lietzke (*17*), Clark, Nabavian, and Bromley (*2*), or of Hickman (*6*), generally are used, although they show substantial deviations and some of them cover only a limited temperature range.

To resolve this contradiction the available experimental vapor pressure measurements on sea water, as reported in the literature, were evaluated, using a recently confirmed rule of additivity of molar vapor pressure depressions. The resulting correlation was used to compare the present calculated data with those of the authors mentioned above. Finally, a table of selected boiling point elevation data is presented in the 20° to 180° C. range for sea water and its concentrates up to threefold concentration.

CALCULATION METHOD

Robinson and Bower's (*13*) additivity rule for relative molal vapor pressure depressions was applied. This method was reliable up to 150° C. on ternary mixtures of the major sea water components (NaCl, KCl, $MgSO_4$, Na_2SO_4); the work is being reported elsewhere (*3*).

The relative molal vapor pressure lowering of a single solute is given as:

$$k = \frac{p^\circ - p}{p^\circ m} \tag{1}$$

where

p° is the vapor pressure of the water at the given temperature
p is the vapor pressure of the solution
m is the molality of the solution

For a mixture of salts, a similar equation can be used:

$$k_m = \frac{p^\circ - p}{p^\circ \Sigma m_i} \tag{2}$$

where

Σm_i represents the total molality of dissolved salts.

The additivity rule can be expressed as:

$$k_m = \Sigma k_i \, x_i \tag{3}$$

where

k_i values are the relative molal vapor pressure depressions of the compounds in a binary solution of the same ionic strength as the mixture
x_i values are the mole fraction of the compounds in the salt mixture ($x_i = m_i / \Sigma m_i$; $x_2 = m_2/\Sigma m_{i \ldots}$)

The k values of the major sea water components were fitted by the method of least squares to a Masson-type equation (*9*) of the form

$$k = a + b\mu^{1/2} \tag{4}$$

where

μ is the ionic strength and a and b are temperature-dependent constants.

The temperature dependence of these constants was expressed by

$$a = a_1 + a_2 t + a_3 t^2 \tag{5}$$

$$b = b_1 + b_2 t + b_3 t^2 \tag{6}$$

Table I gives the constants of Equations 5 and 6 for the major sea water components. The constants for the first four components are based on the authors' measurements (*3*); those for the remaining salts were obtained from the literature (*7, 14*).

By using the described calculation method and constant values given in Table I, two sets of calculations were made. In the first series of calculations, the experimental vapor pressure measurements and boiling point elevations of sea water found in the literature were evaluated. The calculations were based on the actual sea water compositions reported by the individual experimenters. In the second series, the vapor pressure depression and boiling point elevation of a standard sea water were calculated by summing up the vapor pressure depressions of each individual component present in the standard sea water. These calculated boiling point elevation values were then compared with those calculated by other authors.

COMPARISON OF EXPERIMENTAL AND CALCULATED BOILING POINT ELEVATIONS

Experimental values of vapor pressure measurements were obtained from three sources. The measurements of Arons and Kientzler (*1*) covered a narrow temperature range from freezing point up to 25° C. Forrest and Worthley (*4*) reported data between 10° and 100° C., and the measurements of Hara, Nakamura, and Higashi (*5*) ranged from 25° to 175° C. Only the concentration range up to about threefold concentration of the sea water was used in our evaluation.

Table I. Constants for Calculating Relative Molal Vapor Pressure Depressions by Equations 4, 5, and 6

$$k = a + b\mu^{1/2}$$

$$10^3a = a_1 + a_2t + a_3t^2 \quad 10^3b = b_1 + b_2t + b_3t^2$$

	a_1	a_2	$a_3 \times 10^3$	b_1	b_2	$b_3 \times 10^3$	Ref.
NaCl	27.318	0.0851	−0.3813	4.234	−0.0155	0.0189	(*3*)
KCl	29.163	0.0315		2.601	−0.0199		(*3*)
Na_2SO_4	46.583	−0.0294		−6.817	−0.0182		(*3*)
$MgSO_4$	21.334	−0.0232		−1.163	−0.0111		(*3*)
$MgCl_2$	41.518	−0.1505		1.841	0.1891		(*7, 14*)
$CaCl_2$	39.345			8.677			(*14*)
NaBr	31.329			3.193			(*14*)

k = relative molal vapor pressure depression
$a; b$ = temperature-dependent constants
μ = ionic strength
t = temperature, ° C.

Table II. Comparison of Calculated and Experimental Boiling Points of Sea Water and Its Concentrates, ° C.

Chlorinity, 0/00	B. P.		B. P.		B. P.		B. P.		B. P.	
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.
				Arons and Kientzler (*1*)						
5	25.00	24.99								
10	25.00	24.99								
20	25.00	24.97								
30	25.00	24.97								
40	25.00	24.96								
50	25.00	25.00								
60	25.00	25.05								
				Forrest and Worthley (*4*)						
21.26	10.00	10.04	15.00	15.04	20.00	20.07	25.00	25.13	30.00	30.15
73.99	10.00	10.16	15.00	15.32	20.00	20.27	25.00	25.19	30.00	30.22
21.26	35.00	35.05	40.00	40.07	50.00	49.91	100.00	100.42		
73.99	35.00	35.00	40.00	39.96	50.00	49.99	100.00	100.47		
				Hara, Nakamura, and Higashi (*5*)						
19.4	24.97	25.05	49.86	49.81	75.65	75.45	99.19	99.12		
19.87	24.17	24.37	50.18	50.26	75.03	75.01	99.33	99.35		
53.04	24.85	24.93	. . .	. . .	74.09	74.03	100.02	99.85		
19.4	126.14	125.80	150.26	149.97	. . .	. . .				
19.87	125.09	124.94	150.34	150.04	175.22	174.88				
53.04	124.16	123.76	149.24	148.91	176.41	176.00				

Calculated vapor pressure depressions and vapor pressures of the solutions were obtained by the outlined computation technique.

To express the results as boiling point elevations, the boiling point of water corresponding to the vapor pressure of the solution was determined using tabulated water vapor pressure data. The interpolation was made by the Clausius-Clapeyron equation over a 1° C. interval.

The experimentally determined and calculated boiling points are summarized in Table II. From this table, the following conclusions can be drawn.

The data of Arons and Kientzler can be correlated well and with an average deviation of ±0.03° C. Most of the boiling point data of Forrest and Worthley are consistently somewhat lower than the calculated values. Forrest and Worthley noted this deviation when they compared their data with literature values. Finally, the data of Hara, Nakamura, and Higashi are scattered around the correlated data, and even at 25° C. they show excessive deviations for solutions of about the same concentration.

In this evaluation several assumptions had to be made to calculate the composition of the sea water and its concentrates, because these authors did not define exactly the composition of the solutions. Some of the deviations may be attributed to this deficiency.

The correlation used in this evaluation gives a satisfactory average representation of the available data. Any further improvement could be made only with the aid of subjective judgments on the reliability of underlying data.

COMPOSITION OF STANDARD SEA WATER AND ITS CONCENTRATES

Table III gives the basic components of the standard sea water used in our calculations. The first column contains the composition of sea water in parts per million, as given by Spiegler (*16*). The second column shows the equivalent mole per kilogram of water composition, with two minor adjustments. Since there was a slight difference between the total anion equivalents and the total cation equivalents, the potassium molality was reduced by an amount equal to this difference (0.00265). The same procedure was used by Stoughton and Lietzke (*17*). Furthermore, to avoid calculation problems associated with carbonate or hydroxide

Table III. Constituents of Sea Water

	P.P.M.[a]	Molality, *m*
Sodium	10,561	0.47631
Magnesium	1,272	0.05423
Calcium	400	0.01034
Potassium	480	0.01007
Chloride	18,980	0.55511
Sulfate	2,649	0.02979
Bicarbonate	142	
Bromide	65	0.00084

[a] (*16*).

precipitation, the hydrocarbonate content was eliminated by "adding" an equivalent amount of sulfuric acid. The concentration of the sea water concentrates was expressed both by the chlorinity factor (f_{Cl}) which shows the increase of the chlorinity of the sea water (based on 1000 grams of sea water) and by the salt concentration factor (f_s) which follows the increase of the salt content of the water (based on 1000 grams of water). The chlorinity is equal to the total amount of chlorine in grams contained in 1 kg. of sea water after all the bromide and iodide has been replaced by chloride. It is very nearly the concentration of chloride ions in parts per thousand. Both factors (f_{Cl} and f_S) had a value of 1.0 for the original standard sea water of 19.00 chlorinity with a salt content of 35.69 grams of salt per 1000 grams of water.

By increasing temperature and concentration, the solubility limit of calcium sulfate is reached, and precipitation sets in. The amount of calcium sulfate that remained in solution, thus contributing to the vapor pressure depression, was calculated at each level of temperature and concentration. It was assumed that only dihydrate precipitates in the 20° to 100° C. range, and hemihydrate above 100° C. The solubility limits and equilibrium concentrations of calcium and sulfate ions were calculated on the basis of the authors' data and the literature data (*8*, *10–12*, *15*). The ionic compositions of the sea water and its concentrates are given in Table IV.

Table IV. Ionic Composition of Standard Sea Water and Its Concentrates

Moles per kg. of water

Concentration Factor, $\frac{f_{Cl}^{a}}{f_S^{b}}$

	1	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
	1.00000	1.20900	1.442100	1.63600	1.85500	2.07700	2.30200	2.53100	2.76300	2.99900	3.24000
Na^+	0.47631	0.57582	0.07683	0.77938	0.88347	0.98918	1.09651	1.20553	1.31625	1.42873	1.54300
Mg^{-2}	0.05423	0.06556	0.07706	0.08873	0.10059	0.11262	0.12484	0.13725	0.14986	0.16267	0.17568
Ca^{-2}[d]	0.01034	0.01250	0.01469	0.01692	0.01918	0.02147	0.02380	0.02617	0.02857	0.03102	0.03350
K^-	0.01007	0.01217	0.01430	0.01648	0.01868	0.02091	0.02318	0.02549	0.02783	0.03021	0.03262
Cl^-	0.55511	0.67108	0.78880	0.90832	1.02963	1.15282	1.27792	1.40497	1.53400	1.66510	1.79827
SO_4^{-2}[d]	0.02979	0.03601	0.04233	0.04874	0.05526	0.06187	0.06858	0.07540	0.08232	0.08936	0.09650
	0.00084	0.00101	0.00119	0.00137	0.00156	0.00174	0.00193	0.00213	0.00232	0.00252	0.00272
120° C. Ca^{-2}	[c]	[c]	[c]	[c]	[c]	[c]	0.02214	0.02190	0.02153	0.02121	0.02080
SO_4^{-2}	[c]	[c]	[c]	[c]	[c]	[c]	0.06692	0.07113	0.07528	0.07955	0.08380
140° C. Ca^{-2}	[c]	[c]	0.01448	0.01472	0.01478	0.01463	0.01444	0.01418	0.01390	0.01354	0.00940
SO_4^{-2}	[c]	[c]	0.04212	0.4654	0.05086	0.05503	0.05922	0.06341	0.06765	0.07188	0.07240
160° C. Ca^{-2}	0.00871	0.00897	0.00914	0.00198	0.00928	0.00916	0.00900	0.00881	0.00859	0.00836	0.00826
SO_4^{-2}	0.02816	0.03248	0.03678	0.04100	0.04536	0.04956	0.05378	0.05840	0.06234	0.06670	0.07126
180° C. Ca^{-2}	0.00501	0.00513	0.00522	0.00526	0.00528	0.00543	0.00507	0.00494	0.00481	0.00481	0.00452
SO_4^{-2}	0.02446	0.02864	0.03286	0.03708	0.04136	0.04583	0.04985	0.05417	0.05856	0.06300	0.06752

[a] Chlorinity factor. [b] Salt concentration factor. [c] No precipitation occurs below this concentration and temperature limit. [d] At high temperatures, use values given in lower part of this table.

Table V. Boiling Point Elevation of Sea Water and Its Concentrates, ° C.

			Temperature								
			° C. 20	40	60	80	100	120	140	160	180
f_{Cl}[a]	$Cl_{0/00}$[b]	$S_{0/00}$[c]	° F. 68	104	140	176	212	248	284	320	356
1	19.00	34.46	0.30	0.34	0.40	0.47	0.53	0.59	0.66	0.71	0.77
1.2	22.80	41.35	0.36	0.42	0.49	0.57	0.67	0.72	0.80	0.87	0.93
1.4	26.61	48.24	0.43	0.50	0.58	0.68	0.77	0.86	0.95	1.03	1.10
1.6	30.41	55.13	0.51	0.58	0.68	0.79	0.89	1.00	1.10	1.19	1.28
1.8	34.21	62.03	0.57	0.67	0.79	0.90	1.01	1.14	1.26	1.36	1.46
2.0	38.01	68.92	0.65	0.75	0.88	1.02	1.16	1.29	1.42	1.54	1.65
2.2	41.81	75.81	0.72	0.85	0.98	1.13	1.27	1.44	1.58	1.72	1.84
2.4	45.61	82.70	0.81	0.94	1.07	1.26	1.43	1.59	1.75	1.90	2.04
2.6	49.41	89.59	0.89	1.04	1.21	1.39	1.59	1.75	1.92	2.09	2.24
2.8	53.21	96.48	0.98	1.13	1.32	1.52	1.70	1.91	2.10	2.28	2.45
3.0	57.01	103.38	1.06	1.23	1.44	1.66	1.86	2.08	2.28	2.48	2.66

[a] f_{Cl} = Chlorinity factor (multiplying factor of chlorinity). [b] $Cl_{0/00}$ = Chlorinity (parts of equivalent chloride per thousand parts of sea water). [c] $S_{0/00}$ = Salinity (parts of salt per thousand parts of sea water). For ionic composition, see Table IV.

Table VI. Comparison of Calculated Boiling Point Elevations, °C.

Temp., °C.	Weight % Salts																			
	2				4				6				8				10			
	[a]	SL	CNB	H	[a]	SL	CNB	H	[a]	SL	CNB	H	[a]	SL	CNB	H	[a]	SL	CNB	H
25	0.168	0.177	0.16	...	0.357	0.363	0.34	...	0.567	0.564	0.56	...	0.797	0.783	0.79	...	1.048	1.02	...	...
40	0.194	0.198	0.17	0.22	0.411	0.407	0.36	0.45	0.650	0.634	0.59	0.72	0.912	0.882	0.84	1.00	1.196	1.15	...	1.31
60	0.229	0.228	0.17	0.26	0.482	0.470	0.39	0.52	0.761	0.734	0.63	0.81	1.065	1.02	0.91	1.14	1.394	1.34	...	1.50
70	0.246	0.244	0.18	0.33	0.518	0.503	0.39	0.58	0.816	0.785	0.66	0.92	1.141	1.09	0.94	1.22	1.492	1.43	...	1.58
100	0.297	0.295	0.21	...	0.624	0.609	0.44	...	0.981	0.949	0.72	...	1.369	1.32	1.04	...	1.787	1.73	...	...
120	0.331	0.332	0.22	...	0.695	0.685	0.46	...	1.091	1.07	0.77	..	1.521	1.48	1.11	...	1.983	1.94	...	...
140	0.365	0.373	0.23	...	0.765	0.766	0.49	...	1.201	1.19	0.81	...	1.672	1.65	1.17	..	2.178	2.16	...	...

[a] Present work, SL = (*17*), CNB = (*2*), H = (*6*).

BOILING POINT ELEVATION STANDARD SEA WATER

The boiling point elevation of standard sea water, calculated by the method described previously, is given in Table V, and covers the chlorinity increase from $f_{Cl} = 1$ to $f_{Cl} = 3$ in the range 20° to 180° C. The ionic compositions corresponding to each chlorinity factor are given in Table IV.

The boiling point elevation was expressed as a function of temperature and concentration by the method of least squares. Accordingly,

$$\Delta T = Ac + Bc^2 \tag{7}$$

where A and B are temperature-dependent constants

$$A = A_1 + A_2t + A_3t^2 \tag{8}$$

$$B = B_1 + B_2t + B_3t^2 \tag{9}$$

If the concentration is expressed by the chlorinity factor (f_{Cl}), and the temperature is expressed in °C., the values of these constants are:

$A_1 = 0.2009 \times 10^{-3}$ $B_1 = 0.0257 \times 10^{-3}$
$A_2 = 0.2867 \times 10^{-5}$ $B_2 = 0.0193 \times 10^{-5}$
$A_3 = 0.0020 \times 10^{-7}$ $B_3 = 0.0001 \times 10^{-7}$

Table VI gives a comparison of the boiling point elevations at a series of temperatures and concentrations, calculated by the present method, and by the methods of Stoughton and Lietzke (*17*), Clark, Nabavian, and Bromley (*2*), and Hickman (*6*), respectively. The agreement between the results obtained by the present method and that of Stoughton and Lietzke is excellent; the average deviation is about ±0.02° C. The data of Clark *et al.* are too low, and Hickman's data are too high.

The results show that the proposed method yields practically identical results with Stoughton and Lietzke's calculation; in their correlation, the composition of the solution is considered only by the ionic strength and by half the sum of molalities of all ions. In their treatment, all 2–1 and 1–2 electrolytes, and all 2–2 electrolytes, respectively, are assumed to affect the osmotic coefficient and the activity of water to the same extent. In the present correlation, although the calculation is much simpler, the additivity rule is applied individually to all constituents of the solution. Therefore, it is believed that this method could be extended to solutions substantially different in composition from sea water—for example, brackish waters.

The authors' recommended values for sea water boiling point elevations are presented in Table V. The data can be interpolated easily, or Equation 7 renders an easy solution for the calculation.

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