

Osmotic Coefficients of Synthetic Sea-Water Solutions at 25° C.

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The osmotic coefficients of synthetic sea-water solutions and their concentrates at 25° C. have been measured for solutions with ionic strengths from 0.6 to 7. The results indicate that the osmotic coefficient of synthetic sea-water solutions is closely approximated by an equation for the osmotic coefficient of sodium chloride at the same ionic strength with an appropriate correction to the Debye-Hückel contribution for the divalent ions in sea water.

VARIATIONS of free energies from ideality are not only of interest in attempts to understand the properties of solutions, but are of fundamental importance in, among other things, the study of complexing reactions, estimation of molecular weights by such methods as equilibrium ultracentrifugation and light scattering, and the interpretation of kinetic processes including diffusion rates. With respect to aqueous solutions of electrolytic solutes, there is a vast body of data available for two-component systems at 25° C. It is, however, usually systems with more than one solute that in practice are of interest, and, with the major exception of solute pairs which can be studied with reversible electrodes, information concerning three-component solutions is scarce. Harned and Owen (1) have studied extensively pairs containing HCl, and Lanier, (2) using a cation-sensitive glass electrode, has studied pairs containing NaCl. Although estimates might be made from activity coefficients of the limiting two-component systems, in many important cases—e.g., perchlorates—few data are available to provide tests which would make possible a decision concerning the best procedures for computing activity coefficients of multicomponent systems from values of two-component systems.

To help fill this gap, an isopiestic apparatus has been constructed. For the first study of multicomponent systems, solutions having approximately the solute composition of sea water were selected and investigated over a range of ionic strengths. Interest for desalination purposes in boiling point elevations of sea water and its concentrates and in minimum energies of separation of water from solutions has recently led Stoughton and Lietzke (9, 10) to attempt to calculate thermodynamic properties of sea-water solutions from two-component data. It seemed of interest both for practical and theoretical reasons to check their procedure experimentally.

EXPERIMENTAL

Materials. Stock solutions of NaCl were prepared from reagent grade crystals dried overnight at 200° C. The concentrations of the solutions were calculated from the weights of the dried salt. Analysis of these solutions by measurement of the density to five parts in 10⁵ and comparison with the data of Wirth (12) gave differences in molality of 0.08% or less; analysis by precipitation of Cl⁻ as AgCl gave differences in molality of 0.2% or less.

Stock solutions of KCl were prepared from crystals which were purified by recrystallization of reagent grade crystals, drying at 200° C., fusion, and redrying overnight at 200° C. before use. The concentrations of the solutions were calculated from the weights of the dried salt. Analysis of these solutions by precipitation of Cl⁻ as AgCl gave differences in molality of 0.2% or less.

A synthetic sea-water stock solution (I) was prepared containing the ions Na⁺, Mg⁺², K⁺, Cl⁻, and SO₄⁻² in the ratios reported for sea water (8, 10). To obviate the solubility problem, Ca⁺² was replaced by an equivalent amount of Mg⁺², and HCO₃⁻ and Br⁻ by an equivalent amount of Cl⁻. The ions Ca⁺², HCO₃⁻, and Br⁻ are present in minor amounts in sea water, and these substitutions should not have a pronounced effect on the isopiestic ratios. The solution was made by weight from the following: purified NaCl and KCl crystals as described above; a stock solution of MgCl₂ analyzed for Cl⁻ by precipitation of AgCl; a stock solution of Na₂SO₄ analyzed by evaporating aliquots to dryness and further drying at 150° C.; and deionized water. A second stock solution (II), used for the isopiestic run at low concentrations (Run A) was prepared as above except that the NaCl and KCl were added from a single stock solution prepared from reagent grade crystals, the composition of which was calculated from the weights of salts added.

A few results in the low concentration range (Run A) were obtained for synthetic sea-water solutions (III) containing Ca⁺², rather than replacing it with Mg⁺². In this case, the Ca⁺² was added as CaCl₂ from a stock solution analyzed for Cl⁻ by precipitation as AgCl.

The relative composition of these stock solutions and that for "standard sea water" (8, 10) are shown in Table I.

Distilled water, passed through a mixed bed ion exchange column, was used for the preparation of all solutions.

Apparatus and Procedure. The apparatus used for the isopiestic equilibrations was similar to that used by Lindenbaum and Boyd (3). The chamber was machined from Lucite

Table I. Relative Concentrations of Synthetic Sea-Water Stock Solutions

	m_i/m_{Na^+}			
	"Standard Sea Water" ^a	I	II	III
Na ⁺	1	1	1	1
Mg ^{+2c}	0.1139	0.1310	0.1319	0.1099
Ca ^{+2c}	0.0217	0.0212
K ⁺	0.0212	0.0212	0.0211	0.0212
Cl ^{-c}	1.1656	1.1631	1.1649	1.1631
HCO ₃ ^{-c}	0.0051
Br ^{-c}	0.0018
SO ₄ ⁻²	0.0600	0.0600	0.0600	0.0601

^a See References (8) and (10). ^b Solution I was used in Runs B and C; solutions II and III were used in Run A (see Table II).

^c For "standard sea water", Mg⁺² + Ca⁺² = 0.1356 and Cl⁻ + HCO₃⁻ + Br⁻ = 1.1725.

and has an internal diameter of 9 1/4 inches and a height of 4 1/2 inches. The dishes are securely fastened to a gold-plated copper block 1 inch thick and 8 3/4 inches in diameter by means of a socket plate and "bayonet-type" locking threads on the dishes. The socket plate has provision for 12 dishes. The dishes are 1 1/8 inches in diameter and 7/8 inch high and were spun and formed from pure platinum 0.025 inch thick. The inside vertical walls of the dishes were lined with 45-mesh platinum gauze. Covers for the dishes were machined from Teflon. The cover plate of the chamber contains a mechanism for removing and replacing the covers without opening the chamber.

The chamber was immersed in a 500-liter water bath such that the chamber could be rotated around an axis through its center and inclined 20° from the vertical. The dishes, thus, are rotated in a plane tilted 20° from the horizontal; this, combined with the gauze lining in the dishes, appears to provide adequate agitation of the solutions. The temperature of the bath varied 0.003° or less during the course of an equilibration for 18 points, and less than 0.01° for the other three. The temperature of the bath varied from one equilibration run to another within the range of 24.99–25.02° C.

The procedure for evacuating the chamber and sweeping out air was essentially that of Scatchard, Hamer, and Wood (7). In this procedure, a reservoir of approximately the same volume as the chamber is connected between the vacuum pump and the chamber. After the pressure was reduced to approximately 30 mm., further evacuation was achieved by evacuating the reservoir and slowly opening the connection between the reservoir and the chamber. This was repeated 10 times before placing the chamber in the bath for the equilibration. Upon completion of the run, the lids were placed on the dishes, the chamber was removed from the bath, dry air was admitted to the chamber, and the dishes were weighed immediately. Approximately 45 minutes were required to weigh the 12 dishes, with a repeat measurement of the first dish at the end. The differences between the two weighings of the first dish was 0.03% of the weight of the solution, or less. All weights were corrected to vacuum. The dishes were allowed to equilibrate for 2 to 7 days; the longer time was required for the dilute solutions.

The salts were added to the dishes in the form of a solution of approximately the desired concentration for the first equilibration. For subsequent equilibrations, water was added to give the desired concentration. An excess of 0.1 ml. of water was added to one-half of the dishes containing each salt so that equilibrium would be approached from both directions, and the attainment of equilibrium would be indicated by agreement of the concentrations of the two sets. For each set of equilibrations, there were from two to four dishes containing the same salt. For NaCl and sea water, the maximum difference in concentration among the replicate dishes was 0.1% except for the lowest concentration point where the deviation for NaCl was 0.16%. For KCl, the difference was 0.2% or less.

RESULTS AND DISCUSSION

NaCl-KCl. To confirm the adequacy of the equipment and procedure, dishes containing KCl were included in all equilibrations where its solubility permitted. The isopiestic ratio $R_{KCl} = m_{NaCl}/m_{KCl}$ (m is the concentration in moles per kilogram of water) was compared with the values given by Scatchard, Hamer, and Wood (7) and by Robinson (4). The observed ratios agreed with those reported by these authors to ± 0.001 , which is within the scatter of their data.

NaCl-Sea Water. The concentrations of NaCl and synthetic sea water in isopiestic equilibrium are given in Table II. The values shown are the averages of the replicate

Table II. Concentrations of Isopiestic Solutions and Osmotic Coefficients for Sea Water

m_{NaCl}	m_{sw}	ϕ_{sw}
Run A		
1.5795	1.5798	0.9605
1.5498	1.5510	0.9585
1.0188	1.0295	0.9265
0.7785	0.7900	0.9147
0.5056	0.5154	0.9046
Run A (with Ca)		
1.5795	1.5816	0.9594
1.5498	1.5534	0.9570
1.0188	1.0306	0.9255
0.7785	0.7906	0.9140
0.5056	0.5153	0.9048
Run B		
6.0095	5.6848	1.3428
5.7658	5.4666	1.3200
5.3303	5.0748	1.2790
5.1198	4.8860	1.2589
4.4976	4.3182	1.2013
4.0280	3.8892	1.1578
3.5017	3.4032	1.1107
2.9392	2.8788	1.0625
2.4628	2.4295	1.0239
2.1184	2.1009	0.9978
1.8620	1.8547	0.9791
Run C		
2.3529	2.3242	1.0157
2.0277	2.0136	0.9913
1.7443	1.7406	0.9711
1.3061	1.3136	0.9425
1.0506	1.0616	0.9277

dishes. The isopiestic ratio $R_{sw} = m_{NaCl}/m_{sw}$ ($m = \frac{1}{2}\sum m_i$ where m_i is the molality of ion i and the summation is over all the ions) can be represented empirically by the equation

$$R_{sw} = 0.9700 + 0.02006 m_{sw} - 0.00083 m_{sw}^2 \quad (1)$$

with a standard deviation $\sigma = 0.0004$ ($\sigma = [\sum d^2/(n - k)]^{1/2}$ where d is the deviation, n the number of observations, k the number of variable parameters, and the summation is over all observations).

The osmotic coefficients for sea water were calculated from m_{sw} , m_{NaCl} , and ϕ_{NaCl} as follows:

$$\phi_{sw} = \phi_{NaCl} \frac{m_{NaCl}}{m_{sw}} = \phi_{NaCl} R_{sw} \quad (2)$$

with ϕ_{NaCl} given by the following equation derived from the data of Robinson and Stokes (4, 5):

$$\phi_{NaCl} = \phi_{DH} + 0.01842 m + 0.01054 m^2 - 0.000652 m^3 \quad (3)$$

the Debye-Hückel contribution, ϕ_{DH} is given by the following equation (6)

$$\phi_{DH} = 1 - \frac{1.17082 Z}{(a')^3 I} \left[1 + a' I^{1/2} - \frac{1}{1 + a' I^{1/2}} - 2 \ln(1 + a' I^{1/2}) \right] \quad (4)$$

where the charge factor $Z = 1$, the distance of closest approach parameter $a' = 1.5$, and I is the ionic strength on the molality scale. The values of ϕ_{sw} thus obtained are included in Table II and shown in Figure 1 (points) as a function of I_{sw} . For the synthetic sea water solutions used in this work $I_{sw}/m_{sw} = 1.2415$. For convenient interpolation, the following equation has been obtained by a least

squares fit to the experimental values of ϕ_{sw} ; the standard deviation $\sigma = 0.0003$:

$$\phi_{sw} = \phi_{DH} + 0.02212 I + 0.00852 I^2 - 0.000403 I^3 \quad (5)$$

where ϕ_{DH} is given by Equation 4 with $\alpha' = 1.5$ and $Z = \sum v_i z_i^2 / v = I_{sw} / m_{sw} = 1.2415$, where v_i and z_i are the number of and the charge on ion i , v is the total number of ions, and the summation is over all ions.

The osmotic coefficients for solutions in which Ca^{+2} was present agree with those for solutions (Run A) in which it was replaced by an equivalent addition to Mg^{+2} concentration within 0.16% or better (Figure 1, Table II). Substitution for minor sea-water constituents of ions having the same valence does not seem to have an important effect on osmotic coefficients.

Discussion. Stoughton and Lietzke (9, 10) calculated the thermodynamic properties of sea water by, in effect, considering it a perturbed NaCl solution. Specifically, they assumed that osmotic coefficients of sea-water solutions could be calculated from an equation for ϕ_{NaCl} similar to Equation 3, with insertion of the proper valence factor, Z , and the ionic strength in the Debye-Hückel term and insertion of the sea-water concentration in appropriate units in the power series terms (for NaCl, a 1 to 1 electrolyte, I , m , and \mathbf{m} are the same). They tried several different concentration scales for sea water in their equation for

ϕ_{NaCl} , and from comparison of their computed boiling point elevations with what they took to be the best values in the literature, concluded tentatively (9) that the appropriate concentration unit was \mathbf{m} , or one-half the total molality of ions. There is considerable disagreement, however, among values of boiling point elevations of sea water measured in different laboratories, and a direct experimental check seemed desirable.

The semiempirical equation used by Stoughton and Lietzke (10) represented ϕ_{NaCl} over a range of temperatures. Since 25° C. data are of particular interest and a fit applicable only at this temperature is probably better for room temperature than one covering a range of temperatures, Equation 3 (with $Z = 1.2415$ and $\alpha' = 1.5$) has been used in computing ϕ_{sw} with the substitution of different concentration units for m in the power series terms. Figure 1 shows a comparison of curves computed for ϕ_{sw} with concentrations of synthetic sea water expressed as \mathbf{m} (ϕ_1) and as $I(\phi_2)$, with experimental. At least at 25° C., much better agreement between computed and experimental values is obtained by insertion of ionic strength of sea water in Equation 3 for ϕ_{NaCl} than by insertion of \mathbf{m} .

The values of ϕ_{sw} calculated using the equation for ϕ_{NaCl} (Equation 3) compared with the experimental values gave a standard deviation of 0.0034 and a maximum deviation of 0.012.

Stoughton and Lietzke have recently recomputed thermodynamic properties of sea water on this basis (11).

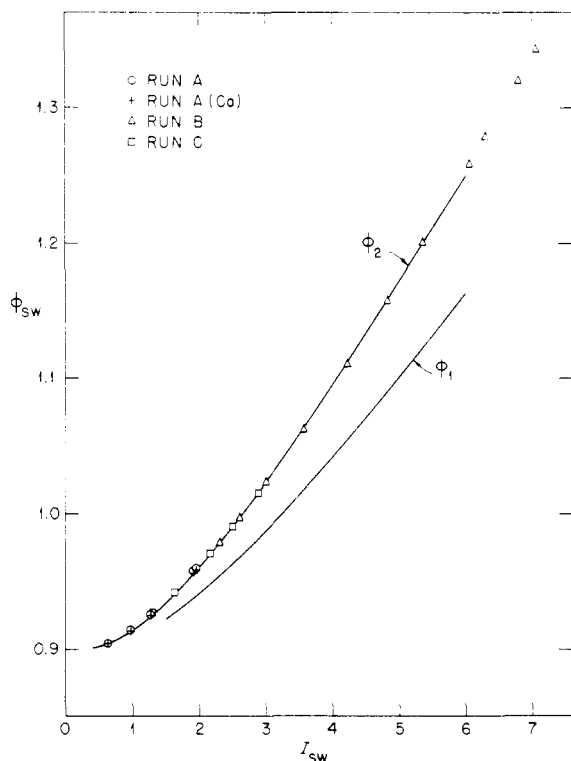


Figure 1. Osmotic coefficients of synthetic sea-water solutions. Calculated curves using concentrations of sea water expressed as $m(\phi_1)$ and $I(\phi_2)$

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