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CALCULATION OF VAPOR PRESSURE OF SEA WATER CONCENTRATES FROM ACTIVITY COEFFICIENT PARAMETERS OF SODIUM CHLORIDE SOLUTIONS

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BRIEF

Activity coefficients of sodium chloride solutions from 25 to 100°C and from 0.05 to 4.0 *m* were used to calculate the vapor pressures of sea salt solutions over the same temperature range and from 1 to 28 wt. % sea salt (about 6 *m* of the mixed salts), by the use of the empirically extended Debye-Hückel equations for the activity and osmotic coefficients. Corrections were made on the limiting slope to adjust it to the average square of the ionic charges. The calculated values were within about 1% of smoothed experimental measurements over the same range of conditions.

In any sea water desalination program involving volatilization it is important to know the vapor pressure of water above the sea salt solution concentrates as a function of temperature and total salt concentration. Higashi, Nakamura and Hara (5) measured the vapor pressure and density of sea salt solutions in the concentration range 3.5 to 28 wt. % of total solids and in the temperature range 0 to 175°C, though not at "round" concentrations or temperatures. Arons and Kientzler (2) measured the vapor pressure of sea salt solutions over the same concentration range as Higashi, Nakamura and Hara but at 5° intervals in the temperature range -10 to +35°C. More recently Gastaldo (3) fitted the data of Higashi, Nakamura and Hara and of Arons and Kientzler to a four parameter equation

$$\ln p = a + b/T + c \ln T + dT. \quad (1)$$

at each experimental concentration. Values of the parameters, *a*, *b*, *c* and *d* were determined at each wt. % of solids from 1 to 28 by the method of least squares on an IBM-7090 computer. In equation 1, *p* is the vapor pressure of water above the solution and *T* is the absolute temperature.

The purpose of the present paper is to demonstrate that the vapor pressures of sea salt solutions can be calculated with reasonable precision over a large concentration and temperature range from the activity coefficients of sodium chloride in NaCl-H₂O solutions. The calculations were carried out with an IBM-7090 computer over the temperature range 25 to 100°C and

from 1 to 28 wt. % total solids. When the vapor pressures calculated in the present work were compared with the values calculated from Gastaldo's parameters, the results of the two calculations agreed about as well with each other as those of Gastaldo did with the experimental data.

METHOD OF CALCULATION

The osmotic coefficient ϕ of a single electrolyte in solution may be defined by equation 2.

$$\nu m \phi \equiv - \frac{1000}{M_w} \ln a_w \quad (2)$$

where *m* is the molality of the solute (moles/1000 grams of solvent), ν is the number of ions per molecule of solute in the standard state (usually the number for complete dissociation), and *a_w* and *M_w* are the activity and molecular weight of the solvent (water in this case). At low pressures (i.e., less than about one atmosphere), the activity of the solvent is approximately equal to the ratio of its vapor pressure over the solution to that over the pure solvent (*p/p_o*).

Equation 2 may be generalized for an electrolyte mixture:

$$\left(\sum_i m_i \right) \phi \equiv - \frac{1000}{M_w} \ln a_w = - \frac{1000}{M_w} \ln \frac{p}{p_o} \quad (2a)$$

where $\sum_i m_i$ is the sum of molalities of all ions.

The method of calculation involved the evaluation of the osmotic coefficients ϕ of the sea salt mixture (at various concentrations and temperatures) from a knowledge of the relative concentrations of ions in "standard" sea water and from known activity coefficients of NaCl in NaCl-H₂O solutions. These values of ϕ were inserted in equation 2a and the corresponding values of the vapor pressure *p* were obtained.

Equations for activity and osmotic coefficients. The

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mean ionic activity coefficient γ_{\pm} and the osmotic coefficient for a single electrolyte were assumed to be given (6) by equations 3 and 4

$$\ln \gamma_{\pm} = \frac{-\rho \sqrt{I}}{1 + A\sqrt{I}} + BI' + CI'^2 + DI'^3 \tag{3}$$

$$\phi = 1 - \frac{\rho \sqrt{I}}{A^2 I} \left[(1 + A\sqrt{I}) - 2 \ln(1 + A\sqrt{I}) - \frac{1}{1 + A\sqrt{I}} \right] + \frac{B}{2} I' + \frac{2C}{3} I'^2 + \frac{3D}{4} I'^3 \tag{4}$$

The first term on the right of equation 3 and the first two terms on the right of equation 4 are the expressions given by the Debye-Hückel theory; I is the ionic strength (on a molality basis); I' is related to the ionic strength (and usually set equal to it for 1-1 electrolytes); B , C and D are adjustable parameters (which may be evaluated from either osmotic or activity coefficient data (6)). In the Debye-Hückel expression ϕ is the limiting-slope, ρ is the density of the solvent, and A is an adjustable parameter which is often set equal to 1.5 independent of temperature (8). The factor $\rho^{1/2}$ corrects molality to molarity as required by the Debye-Hückel theory.

The limiting slope ϕ varies inversely as the product of the dielectric constant D of the solvent and the absolute temperature T raised to the 3/2 power and depends on the square of the charges of the ions under consideration. The temperature variation of D with T was assumed to be that given by the equation of Akерlof and Oshry (1).

$$D = 5321/T + 233.76 - 0.9297 T + 0.001417 T^2 - 8.292 \times 10^{-7} T^3 \tag{5}$$

By the use of equation 5 the limiting slope for an ion of unit charge (or for $\ln \gamma_{\pm}$ of a 1-1 electrolyte) at any temperature may be expressed in terms of the value at 25°C by equation 6

$$\phi_1 = 1.17202 (D_{25} T_{25}/DT)^{3/2} \tag{6}$$

For the sea water mixtures the limiting slope becomes

$$\phi = \frac{\sum m_1 Z_1^2}{\sum m_1} \phi_1 \tag{7}$$

where m_1 and Z_1 represent the molality and charge of any ion constituent. The ionic strength I is defined by equation 8

$$I = \frac{1}{2} \sum m_1 Z_1^2 \tag{8}$$

and hence depends on the concentrations of the ionic constituents. The ionic concentration function I' was set equal separately to three different expressions which are equal for uni-univalent electrolytes.

$$I' = \frac{1}{2} \sum m_1 Z_1^2 = I \tag{9a}$$

$$= \frac{1}{2} \sum m_1 |Z_1| \tag{9b}$$

$$= \frac{1}{2} \sum m_1 \tag{9c}$$

Evaluation of parameters B, C and D for NaCl. With the value of A in equation 3 set equal to 1.5 at each temperature values of B , C and D in equation 3 were evaluated by the method of least squares from literature values for the activity coefficient of NaCl up to 4 *m*. For 25 and 40°C values of the NaCl activity coefficients (for NaCl-H₂O solutions) were taken from Harned and Owen (4), while the values at 60, 80 and 100°C were taken from the text of Robinson and Stokes (7). The values of the parameters B , C and D so obtained are given in Table 1.

Table 1
Parameters B, C and D of Equation 2 for NaCl

t(°C)	B × 10 ²	C × 10 ²	D × 10 ³
25	2.4139	2.2937	-1.9678
40	4.1790	2.1115	-1.9747
60	5.8871	2.1478	-2.5538
80	6.5890	1.6179	-1.8638
100	6.1676	1.8612	-2.3089

Osmotic coefficients and vapor pressures of sea salt solutions. The composition of "standard" sea water was taken from Spiegler (9) and is shown in Table 2.

Table 2
Major Constituents of Sea Water
(in parts per million)

Sodium (Na ⁺)	10,561
Magnesium (Mg ⁺⁺)	1,272
Calcium (Ca ⁺⁺)	400
Potassium (K ⁺)	380
Chloride (Cl ⁻)	18,980
Sulfate (SO ₄ ⁻)	2,649
Bicarbonate (HCO ₃ ⁻)	142
Bromide (Br ⁻)	65
Other solids	34
Total dissolved solids	34,483
Specific gravity (20° C)	1.0243
Water (balance)	965,517

On converting the concentrations given in Table 2 to a molality basis the limiting slope for a sea salt mixture becomes 1.2457 ϕ_1 according to equation 7. The three values for $2I'$ (equations 9a,b,c) for "standard" sea water (total dissolved solids 3.448 wt. %) are 1.4156, 1.2295 and 1.1364.

Values of osmotic coefficients for sea salt solutions from 1 to 28 wt. % dissolved solids were calculated from 25 to 100°C for each of the three expressions for I' (equations 9a,b,c) by using equation 4 and the parameters in Table 1. The value of the parameter A was set equal to 1.5 at each temperature. The limiting slope was evaluated by the use of equations 5, 6 and 7 at each temperature.

Vapor pressures of the sea salt solutions were calculated for each value of ϕ by using equation 2a.

RESULTS AND DISCUSSION

The vapor pressures $p_{(9c)}$ of the sea salt solutions calculated by using the expression for I' as defined in equation 9c are given in Table 3 along with the values obtained with Gastaldo's equation, p_G . The values of

Table 3
Calculation of Vapor Pressure (in atm.) of Sea Salt Solutions from Activity Coefficient Data

Wt. % Solids	t(°C)									
	25		40		60		80		100	
	P _G	P _(9c)	P _G	P _(9c)	P _G	P _(9c)	P _G	P _(9c)	P _G	P _(9c)
1	0.0311	0.0311	0.0725	0.0725	0.1957	0.1957	0.4653	0.4651	0.9956	0.9950
5	.0305	.0304	.0711	.0709	.1923	.1913	.4578	.4546	.9812	.9728
10	.0294	.0294	.0686	.0685	.1858	.1847	.4429	.4392	.9505	.9399
15	.0282	.0282	.0657	.0656	.1780	.1767	.4250	.4205	.9138	.9000
20	.0268	.0267	.0623	.0620	.1687	.1672	.4030	.3981	.8676	.8528
25	.0250	.0249	.0583	.0579	.1577	.1568	.3770	.3731	.8125	.8011
28	.0238	.0238	.0553	.0553	.1498	.1507	.3578	.3578	.7706	.7713

the vapor pressure calculated by using I' as given by equation 9c are somewhat closer to those given by equation 1 than are those obtained by the use of equation 9b; the latter are in turn somewhat closer to Gastaldo's values than are those resulting from the use of equation 9a. See Table 4. It is not known whether the expression for I' given by equation 9c is in general better than the expressions given by equations 9b or 9a for calculations of this sort, or whether equation 9c compensates better for the fact that while the values of B , C and D were obtained for "pure" NaCl solutions they were used here for sea salt mixtures. In any case the agreement between observed and calculated pressures is good, being generally about as good as the differences between the pressures calculated from Gastaldo's equation 1 and the experimental data. In all but a very few cases the calculated pressures (equations 2a) were lower than those given by equation 1, indicating a bias either in the observed vapor pressures or (more likely) in the assumptions made here. Gastaldo's coefficients were made to fit the data in the least square's sense and therefore the vapor pressures calculated by using equation 1 show both

Table 4
Average % Difference* Between Water Vapor Pressure Calculated from Eq. 1 and from Eqs. 2a, 4 and 9a, b or c

t(°C)	Average % Difference		
	Eq. 9a	Eq. 9b	Eq. 9c
25	0.59	0.37	0.22
40	.62	.45	.30
60	.96	.68	.56
80	1.02	.79	.70
100	1.34	1.08	.97

* Sum of magnitudes of % difference divided by number of concentrations (i.e., divided by 7).

positive and negative differences from the experimental values.

It is interesting to note that while the parameters B , C and D were evaluated from activity coefficient values of NaCl at 16 concentrations (7) up to 4 *m* (about 20 wt. %) at 60, 80 and 100°C, the calculated vapor pressures for the salt mixtures at those tempera-

tures were within about 1% of Gastaldo's values up to 28 wt. % (over 6 *m*). The questions arose as to the effect on vapor pressure calculations (a) of using activity coefficient values of NaCl at few concentrations to evaluate the parameters B , C and D , and (b) of terminating equations 3 and 4 with quadratic rather than cubic terms (i.e., of evaluating only a B and C parameter with D set equal to zero). The following calculations were carried out to elucidate this question.

Values for the parameters B , C and D (equation 3) were evaluated by using only 10 data points at each temperature (0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 *m*) rather than the 16 given (0.05 to 4.0 *m*) in ref. (7). The results were about the same as those presented above except for the 100°C calculations which involved an extrapolation beyond 4 *m* (i.e., above about 20 wt. %). At 28 wt. % solids at 100°C the deviations of the calculated vapor pressures from Gastaldo's values were 35, 16 and 11% for calculations based on equations 9a, 9b and 9c, respectively.

Calculations were then carried out in which the power series in I' in equations 3 and 4 were terminated

with the quadratic rather than the cubic term. When NaCl activity coefficients at only 10 concentrations were used at each temperature to evaluate B and C , the average deviations varied from 0.8 to 4.0% with a maximum of 12% (equation 9a) and 6% (equation 9c) at 28 wt. % sea salt at 100° C; when activity coefficients at 16 concentrations were used the average deviations varied from 0.7 to 2.6% with a maximum of about 6.5% (equation 9a) and about 2.8% (equation 9c) at 28 wt. % at all temperatures.

The results reported here indicate that the vapor pressure of "standard" sea salt solutions may be calculated to within about 1% under the conditions where activity coefficients of NaCl are known. Even with moderate deviations from the "standard" composition it is felt that such vapor pressures can be calculated to 100° C to within this accuracy. Equation 9c should be used for the functional form of I' .

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NEWS OF TENNESSEE SCIENCE

The University of Tennessee Department of Botany has received a \$4,356 grant from the National Cancer Institute Division of the U. S. Department of Health, Education, and Welfare, to sponsor research under the direction of Dr. Sandra L. Bell, Associate Professor of Botany.

According to Dr. Bell, "The purpose of the research program is to determine the cellular effects of a chemical, fluorodeoxyuridine, which causes mutations and chromosome breakage in the broad bean."

This chemical has been used in the treatment of advanced forms of cancer in the human body. Research is simplified by performing experiments with plants and the results are correlated with the more complex human system.

The University of Tennessee Department of Bacteriology has received a \$39,410 grant from the U. S. Department of Health, Education and Welfare to help finance research concerning the probability of botulism contamination in the TVA lakes.

The three year research study, under the direction of Dr. D. Frank Holtman, Head of the UT Department of Bacteriology, will determine the existence or non-existence of the deadly poisonous botulism organism in the TVA lakes. If the organisms do exist in the mud or water of a lake, their concentration and effects will also be studied.

The necessity of this research was outlined at a two-day symposium on botulism in Cincinnati early this year following deaths in Knoxville and Nashville from

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botulism poisoning traced to canned fish from the Great Lakes region. Similar research is now under way at the University of Wisconsin to check into the possible presence of the botulism organism in the Great Lakes, which might be the original source of the fish contamination.

Ten state universities in the South have agreed to pool the faculties and facilities of their colleges of pharmacy to improve graduate education in the pharmaceutical sciences.

Signing of the agreement by the presidents of the institutions has been announced jointly by Dr. Finfred L. Godwin of Atlanta, Director of the Southern Regional Education Board, and Dr. Seldon D. Feurt, Dean of the University of Tennessee College of Pharmacy.

Dr. Feurt, Chairman of the Southern Council of Graduate Pharmaceutical Education, said pooling of the talents and resources of the institutions involved will be achieved by an exchange of graduate students and summer seminars, etc., by the faculties of the participating universities. The program will be conducted under the auspices of the Southern Regional Education Board.

State universities involved in the agreement were Arkansas, Florida, Georgia, Maryland, Mississippi, North Carolina, South Carolina, Texas, Medical Colleges of Virginia and the University of Tennessee.

(Continued on Page 116)