$t$ = temperature, °C
$V$ = liquid molal volume of pure component
$x$ = mole fraction in liquid phase
$y$ = mole fraction in vapor phase

GREEK LETTERS

$\beta_{11}, \beta_{22}$ = second virial coefficient of pure components 1 and 2, respectively
$\beta_{12}$ = cross second virial coefficient
$\gamma$ = activity coefficient
$\gamma^{\infty}$ = activity coefficient at infinite dilution
$\delta$ = defined in Equation 2

SUBSCRIPTS

1, 2, $i$, $j$ = components

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# Vapor-Liquid Equilibria of Synthetic Seawater Solutions from 25–100°C

H. FRANK GIBBARD, JR.,[1] and GEORGE SCATCHARD
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139

**The vapor pressures of synthetic seawater solutions have been measured at ionic strengths of 1.0, 2.8, and 5.8 from 25–100°C. The approximate equation for the osmotic coefficient tested by Rush and Johnson at 25°C is less accurate at higher temperatures but predicts osmotic coefficients of synthetic seawater solutions within 1.5% even at 100°C. Calculations by the "ion-component" treatment of Scatchard fit the experimental values up to 2.8*m* within a few tenths of 1% over the whole range of temperatures.**

The behavior of seawater and its concentrates is of considerable practical interest at present because of its relation to desalination. Seawater is of more interest to the authors as a complex electrolyte mixture whose properties may be used to test theoretical mixture equations. A very simple equation proposed by one of us (G. S.) predicts the osmotic coefficients of synthetic sea salt solutions from those of sodium chloride solutions at the same ionic strength. Rush and Johnson (*16*) tested this isopiestically at 25°C and found that it holds remarkably well. Having already made precise vapor pressure measurements on aqueous sodium chloride (*6*) from 25–100°C, we decided to measure the vapor pressures of a few synthetic seawater solutions over the same temperature range.

## EXPERIMENTAL

**Materials.** Reagent-grade salts were used without purification, except that powdered sodium chloride and potassium chloride were dried overnight at 165°C. Stock solutions of magnesium chloride and sodium sulfate were prepared and analyzed gravimetrically as silver chloride and barium sulfate, respectively. Triplicate analyses gave average deviations of less than 0.05% in the molality for both stock solutions. Doubly distilled conductivity water was used in the preparation of all solutions.

A stock solution of synthetic seawater containing $Na^+$, $K^+$, $Mg^{2+}$, $Cl^-$, and $SO_4^{2-}$ ions in the proportions used by Rush and Johnson (*16*) was prepared. The relative concentrations of the ions are shown in Table I. The composition differs from that of "standard seawater" (*26*) by the replacement of bicarbonate and bromide by chloride and the replacement of calcium by magnesium.

**Apparatus.** The static vapor pressure apparatus used in this work resembles the apparatus of Scatchard et al. (*24*) but differs considerably from theirs in the details of its construction and operation. These details will be reported else-

Table I. Relative Proportions of Ions in Synthetic Seawater Stock Solution

| Ion | $m_i/m_{Na^+}$ (this work) | $m_i/m_{Na^+}$ (*16*) |
|---|---|---|
| $Na^+$ | 1 | 1 |
| $Mg^{2+}$ | 0.1313 | 0.1310 |
| $K^+$ | 0.0212 | 0.0212 |
| $Cl^-$ | 1.1638 | 1.1631 |
| $SO_4^{2-}$ | 0.0600 | 0.0600 |

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[1] Present address, Department of Chemistry, Southern Illinois University, Carbondale, Ill. 62901. To whom correspondence should be addressed.

**Table II. Osmotic Coefficients of Synthetic Seawater Solutions**

| | Run 3 | | Run 2 | | Run 1 | |
|---|---|---|---|---|---|---|
| $t$, °C | $I$, mol/kg | $\phi$ | $I$, mol/kg | $\phi$ | $I$, mol/kg | $\phi$ |
| 25.0 | 1.013 | 0.918 | 2.799 | 1.016 | 5.788 | 1.225 |
| 37.5 | 1.013 | 0.921 | 2.800 | 1.020 | 5.789 | 1.242 |
| 50.0 | 1.013 | 0.920 | 2.800 | 1.020 | 5.790 | 1.227 |
| 62.5 | 1.014 | 0.915 | 2.801 | 1.014 | 5.791 | 1.207 |
| 75.0 | 1.014 | 0.917 | 2.802 | 1.011 | 5.795 | 1.193 |
| 87.5 | 1.015 | 0.909 | 2.804 | 1.003 | 5.801 | 1.179 |
| 100.0 | 1.016 | 0.903 | 2.807 | 0.994 | 5.807 | 1.159 |

where (*21*). The apparatus operates with a precision of 0.002° and 0.005 torr. The temperature range is 25–100°C.

**Procedure.** The degassing procedure used in earlier work with single salts (*6, 20, 21*) began with the dry salt and could not be used for the sea salt work. The solutions were degassed by repeatedly expanding off the water vapor from the vapor space of the cell while the solution was stirred at 75°C. The degassing process required five to seven days or more before no residual permanent gas could be detected in the vapor. Water lost during degassing was replaced by the distillation of an equal amount of thoroughly degassed water from a reservoir into the vapor pressure cell.

The experimental procedure after the completion of degassing was the same as that used earlier (*6, 21*). After the last measurement, the cell was cooled to 25°C and all the solution removed with a hypodermic syringe. The solution was weighed and analyzed gravimetrically as silver chloride to give the low-temperature composition. Because of evaporation into the vapor space, the concentration is about 0.1% greater at 75°C, and 0.3% greater at 100°C, than at 25°C. The concentration is determined precisely for each temperature from the total volume minus that of the liquid. All solution weights are corrected to vacuum. The usual pressure corrections are made for capillary depression of mercury in the manometer tubes, hydrostatic pressure heads, thermal expansion of the invar comparator scale, and reduction to standard gravity and to mm Hg at 0°C.

The activity of the water $a_w$ in a solution is determined by correcting the ratio of the vapor pressure to that of pure water for the deviation from perfect gas behavior. The osmotic coefficient $\phi$ is determined through its definition

$$\phi = -(1/\Sigma_i m_i)\ 55.51 \ln a_w \tag{1}$$

in which $\Sigma_i m_i$ is the stoichiometric concentration of all ionic species.

## RESULTS AND DISCUSSION

The experimental osmotic coefficients and ionic strengths, expressed in moles of solute per kilogram of water, are given in Table II. Qualitatively the behavior of the osmotic coefficients resembles that of sodium chloride solutions (*6, 8, 21*) which is not surprising because of the high concentrations of sodium and chloride ions relative to the other ions in seawater. At a fixed ionic strength, the osmotic coefficient passes through a maximum between 30° and 60°C, and the position of the maximum shifts to lower temperatures with increasing concentration (Figure 1).

**Calculation of $\phi_{SW}$ from Sodium Chloride Parameters.** In 1961 Scatchard (*20*) suggested that the osmotic coefficients of an electrolyte mixture could be expressed as the sum of a Debye-Hückel term and an integral power series in the ionic

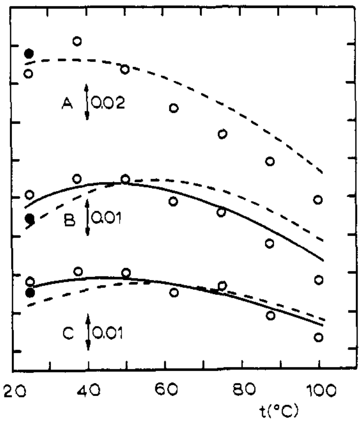

Figure 1. Osmotic coefficients of synthetic seawater solutions

Open circles, this work; filled circles, results of Rush and Johnson. Ordinates are arbitrarily displaced. Nominal ionic strengths: A, 5.8; B, 2.8; C, 1.0. Full curves, ion-component treatment; broken curves, approximate equation from NaCl parameters

**Table III. Parameters for Osmotic Coefficient Calculations**

| | NaCl | $MgCl_2$ | $Na_2SO_4$ | $MgSO_4$ |
|---|---|---|---|---|
| $a$ | 1.500 | 1.750 | 1.241 | 1.375 |
| $b^{(1,0)}$ | 0.01644728 | 0.074488 | −0.09870 | −0.10850 |
| $b^{(1,1)}$ | −3366.4808 | −147.8284 | −70.5590 | 0 |
| $b^{(1,2)}$ | −26.959273 | −0.5888 | 0 | 0 |
| $b^{(1,3)}$ | 0.18020612 | 0 | 0 | 0 |
| $b^{(1,4)}$ | −0.0000348307 | 0 | 0 | 0 |
| $b^{(2,0)}$ | 0.01115840 | 0.0309258 | 0.0163417 | 0.03370 |
| $b^{(2,1)}$ | 1883.61137 | 3.18099 | 8.14665 | 0 |
| $b^{(2,2)}$ | 16.186802 | 0 | 0 | 0 |
| $b^{(2,3)}$ | −0.04666187 | 0 | 0 | 0 |
| $b^{(2,4)}$ | 0.0000224378 | 0 | 0 | 0 |
| $b^{(3,0)}$ | −0.000716277 | −0.00211957 | −0.0006564 | −0.0015192 |
| $b^{(3,1)}$ | −286.344718 | −0.0864393 | 1.08777 | 0 |
| $b^{(3,2)}$ | −2.5374860 | 0 | 0 | 0 |
| $b^{(3,3)}$ | 0.007502420 | 0 | 0 | 0 |
| $b^{(3,4)}$ | −0.000003693001 | 0 | 0 | 0 |

$s_0 = 1.17284$
$s_1 = 6260.357$
$s_2 = 54.42507$
$s_3 = -0.1619930$
$s_4 = 0.00008596064$

strength $I$. For the coefficients in the power series in $I$ for sea salt solutions Rush and Johnson (*16*) tried substituting the corresponding coefficients for sodium chloride solutions. They found that this simple procedure predicts osmotic coefficients of synthetic seawater at 25°C within a few tenths of 1% for ionic strengths of 0.6 to 7.

To test the simple equation for synthetic seawater at temperatures above 25°C, we write for the osmotic coefficient

$$\phi = 1 - 2\,SZI/a'\Sigma_i m_i + (1/2)\Sigma_j B^{(j)} I^j \qquad (2)$$

where $-S$ is the Debye-Hückel slope for $\ln \gamma_\pm$ of a uni-univalent electrolyte, $a'$ is the ion size parameter, and $Z$ is defined by

$$Z = [1 + a'I^{1/2} - 1/(1 + a'I^{1/2}) - 2 \ln (1 + a'I^{1/2})]/a'^2 I \qquad (3)$$

For our synthetic seawater $2\,I/\Sigma_i m_i = 1.2416$, and $a'$ is taken to be 1.5. The $B$'s and $S$ are functions of temperature which take the following form if the excess enthalpy is expressed as a Taylor's series about a standard absolute temperature $T_s$, (*5*) which we choose as 298.15K.

$$S = s_0 + s_1(1/T - 1/T_s) + s_2 \ln T/T_s + s_3(T - T_s) + s_4(T^2 - T_s^2) \qquad (4)$$

$$B^{(i)} = b^{(i,0)} + b^{(i,1)}(1/T - 1/T_s) + b^{(i,2)} \ln T/T_s + b^{(i,3)}(T - T_s) + b^{(i,4)}(T^2 - T_s^2) \qquad (5)$$

The $b$ parameters listed for sodium chloride in Table III are taken from an equation developed to fit the sodium chloride vapor pressure results of Gibbard (*6, 21*), Olynyk and Gordon (*11*), Frazer (*3*), Negus (*10*), and Gardner et al. (*4*) and the freezing point results of Scatchard and Prentiss (*22*). The $s$ parameters are taken from an equation derived from the dielectric constants (*1, 12*) and densities, taken from the International Critical Tables, of water.

The osmotic coefficients calculated from Equations 2–5 and the parameters of Table III are shown as the broken curves in Figure 1. The agreement of the experimental values with the calculated values and with the values calculated from Equation 5 of Rush and Johnson (*16*) is excellent at 25°C. At higher temperatures the differences between the calculated and experimental values increase but do not exceed 1.5% even at an ionic strength of 5.8. The appropriate question is not why the simple equation works less well at 100 than at 25°C, but rather, in view of its simplicity, why it works so well at 25°C. Both questions can be answered by application to synthetic seawater of the "ion-component" treatment of electrolyte mixtures (*18, 19*).

**Calculation of $\phi_{SW}$ by Ion-Component Treatment.** In applying the ion-component treatment to synthetic seawater, we replace potassium ion by sodium ion in the calculations. This introduces an error of only about 0.001 in $\phi_{SW}$ for ionic strengths of 0–2.8$m$. The ion-component equation used for synthetic seawater is

$$\phi = 1 + (1/\Sigma_i x_i/z_i)\Big\{\sum_a{}^{+}\sum_f{}^{-}[x_a x_f(z_a + z_f)Z_{af}S/a'_{af} + x_a x_f(B_{af}{}^{(1)}m' + B_{af}{}^{(2)}m'^2 + B_{af}{}^{(3)}m'^3)] + \sum_a{}^{+}\sum_b{}^{+}\sum_f{}^{-} x_a x_b x_f(B_{af}{}^{(0,1)}m' + B_{abf}{}^{(0,2)}m'^2 + B_{abf}{}^{(0,3)}m'^3) + \sum_a{}^{+}\sum{}^{-}\sum_g{}^{-} x_a x_f x_g(B_{fg}{}^{(0,1)}m' + B_{afg}{}^{(0,2)}m'^2 + B_{afg}{}^{(0,3)}m'^3)\Big\} \ldots \qquad (6)$$

where
the sums are taken over cation species $a$ and $b$ and anion species $f$ and $g$; $z_i$ is the absolute value of the valence of the ion species $i$; $Z$ is defined by Equation 3, with a different value of $a'$ for each pair of ions $af$; and $m'$ and $x_i$ are the total equivalent concentration and the equivalent fraction of species $i$, respectively, defined by $m' = (1/2)\ \Sigma_i m_i z_i$ and $x_i = m_i z_i/m'$. For our synthetic seawater, the equivalent fractions of the ions are: $Na^+$, 0.79545; $Mg^{2+}$, 0.20450; $Cl^-$, 0.90650; $SO_4{}^{2-}$, 0.09355.

The $a'$ and $B^{(i)}$ parameters are evaluated by the method of least squares from the osmotic coefficients of two-ion solutions. The temperature dependence of the $B^{(i)}$ parameters is given by Equation 5. The determination of the parameters listed in Table III for each salt is discussed below.

**NaCl.** The contribution to $\phi_{SW}$ from the term of Equation 6 with $a$ = Na and $f$ = Cl is by far the largest. Fortunately sodium chloride is also the salt for which the most extensive and accurate results are available. The equation of Scatchard and Gibbard, discussed in the section on calculations based on sodium chloride parameters, also provides the basis of the ion-component calculations.

**$MgCl_2$.** The freezing point results of Gibbard and Gossmann (*7*), the isopiestic results of Wu et al. (*27*) and Platford (*14*), and the 20°C heat capacities of Eigen and Wicke (*2*) were used. The limited concentration range of Eigen and Wicke's results permits the determination of $b^{(1,2)}$ but not $b^{(2,2)}$ or $b^{(3,2)}$. The calculations for $I = 2.8$ require a considerable extrapolation; calculations for higher concentrations are not justified.

**$Na_2SO_4$.** The isopiestic results of Lietzke and Stoughton (*9*) and of Robinson and Stokes (*15*) at 25°C and of Soldano and co-workers (*13, 25*) at 100 and 121°C were used to determine the $b^{(i,0)}$ and $b^{(i,1)}$ parameters.

**$MgSO_4$.** Because of the very small contribution to $\phi_{SW}$ from the term with $a$ = Mg and $f$ = $SO_4$, a very crude approximation to the temperature dependence of the $B^{(i)}$ parameters is satisfactory. The 25°C parameters determined from isopiestic measurements (*9, 15*) were used at all temperatures.

The values of the $B^{(0,i)}$ parameters were taken from the calculations on the three-ion mixtures by Scatchard et al. (*23*). The contribution to $\phi_{SW}$ from the sum over three ions does not exceed 0.0075 at 25°C and is assumed to be independent of temperature.

The osmotic coefficients calculated by the ion-component treatment are shown by the full curves in Figure 1. For temperatures above 50°C, the ion-component treatment gives a considerably more accurate prediction of $\phi_{SW}$ than the simple Equation 2. The deviations of the experimental points from the full curves increase with temperature; this is probably due to the crudeness of the approximations used for the temperature dependence of the osmotic coefficients of magnesium chloride and sodium sulfate.

The contribution to $\phi_{SW}$ from the non-Debye-Hückel part of the osmotic coefficient is large and positive for magnesium chloride and large and negative for sodium sulfate. Near 50°C the two contributions tend to cancel, and the approximate Equation 2 is quite accurate. At temperatures much above or below 50°C, the cancellation does not occur to the same extent, and the approximate equation is less accurate. Thus the good agreement of Equation 2 with experimental values at 25°C is largely fortuitous.

The ion-component treatment predicts osmotic coefficients of synthetic seawater within 0.005 for ionic strengths up to 2.8 (about a four-fold concentration of natural seawater). It is unlikely that more accurate osmotic coefficients would be required for any practical purpose. To extend the computations to higher concentrations would require measurements of the osmotic coefficients or heats of dilution and heat capacities of magnesium chloride and sodium sulfate from 25–100°C.

Many properties related to the osmotic coefficient (e.g., boiling point elevations, heats and free energies of vaporization of water, activity coefficients) may be calculated from Equation 6 with the parameters of Table III, but these calculations lie outside the scope of this article.

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# Thermodynamic Properties of Some Cycloalkane–Cycloalkanol Systems at 25°C

DAVID E. G. JONES,[1] IAN A. WEEKS,[2] SUBHASH C. ANAND, ROSS W. WETMORE, and GEORGE C. BENSON[3]
Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A OR6

**Molar excess enthalpies and volumes of the systems cyclopentane–cyclopentanol and cyclohexane–cyclohexanol at 25°C were determined by direct calorimetric and dilatometric measurements. Excess Gibbs free energies (also at 25°C) were obtained from studies of the vapor-liquid equilibria. Correlation of the results for the excess enthalpy and free energy by means of the NRTL theory was investigated.**

There have been few previous investigations of the thermodynamic properties of binary mixtures formed from cycloalkanes and cycloalkanols. This paper reports measurements of excess enthalpies, excess volumes, and vapor-liquid equilibria for the systems cyclopentane–cyclopentanol and cyclohexane–cyclohexanol at 25°C.

## EXPERIMENTAL

Only a brief outline of the equipment and operational methods is given below. More detailed descriptions can be found in previous publications. Although the freezing temperature of cyclohexanol is about 25.4°C (*23*), it was possible to carry out the determinations of $H^E$ and $V^E$ at 25°C with this component in a supercooled liquid state.

**Calorimetric Measurements.** A modified form of Van Ness dilution calorimeter (*15*) was used to determine the excess enthalpies. In this calorimeter, successive measured portions of one component were added to a weighed amount of the other component in the absence of any vapor space. The cooling effect of the mixing process was compensated by Joule heating, and the electrical energy needed to maintain a set value of the temperature in the mixing vessel was determined. Generally, variations of the temperature from the set value were less than ±0.003°C, and there was close compensation between positive and negative deviations. At the completion of a dilution, the temperature was restored to within ±0.0003°C of the set value. The calorimeter was immersed in a water bath operated at 25.00 ± 0.01°C and controlled to ±0.001°C during a run. The error of the enthalpy results for the present systems is estimated to be less than ±1% over most of the concentration range.

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[1] Present address, Department of Chemistry, University of Otago, Dunedin, New Zealand.
[2] Present address, Division of Applied Chemistry, C.S.I.R.O., Melbourne, Australia.
[3] To whom correspondence should be addressed.