or fraction
x^* = x in equilibrium with y
y = concentration m.v.c. in vapor phase, mole percent or fraction
σ = surface tension, dyn/cm

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Ion Pair Formation Model for Sea Salt Solutions

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Data on thermodynamic properties of sea salt solutions along with the correlations to obtain these properties have been published by the authors in a previous paper (Bromley et al., 1974. Those correlations are not entirely satisfactory in the sense that no physical insight is provided. The main constituent of sea salt is NaCl. The properties of sea salt solutions, however, differ considerably from those of NaCl solutions due to the presence of appreciable quantities of bivalent ions, Ca^{++}, Mg^{++}, $SO_4^{=}$. Previous workers have observed that the $SO_4^{=}$ ion has a strong tendency to form ion pairs with bivalent cations, particularly with Mg^{++} and Ca^{++} ions. A simple model using the idea of pair formation has been worked out. Predictions based on this model are in very good agreement with the available experimental data.

DESCRIPTION OF THE MODEL

It has been assumed that the ion pair formation takes place primarily between the bivalent cations and anions and that all these pair formations may be represented by a single equivalent reaction

$$M^{++} + X^{=} \rightleftharpoons MX \tag{1}$$

where M^{++} represents the sum total of all the bivalent cations and $X^{=}$, the sum total of all the bivalent anions present in sea salt. The ions that are removed to form the uncharged species, contribute little to the charge distribution or potential. An individual ion in the solution does not see any net electrical charge on the pair. Also, the number of particles in the solution is less than in the case where no such pair formation occurs. Thermodynamic properties are usually reported on the basis of total number of ions assuming no pair formation. Hence two sets of thermodynamic quantities can be defined. The first set is defined assuming no pair formation and is referred to as *stoichiometric*. The second view takes pair formation into account and is referred to as *microscopic*. The first set is denoted by the subscript *stoi*. In the following discussion the terms without this subscript pertain to the second set.

The equilibrium constant for pair formation can now be written as

$$K = \frac{m'\gamma'}{(m_{++}\gamma_{++})(m_{=}\gamma_{=})} \tag{2}$$

In order to obtain an expression for the stoichiometric activity coefficient, the following assumptions are made:

1. The activity coefficient of the pair species γ' is unity.
2. The activity coefficients γ_{++} and $\gamma_{=}$ can be adequately approximated by the Debye-Hückel term, that is,

$$\ln \gamma_{++} = \ln \gamma_{=} = -2.303\, A\gamma (2)^2 \frac{I^{1/2}}{1 + I^{1/2}} \tag{3}$$

3. The microscopic mean ionic activity coefficient is given by the correlation proposed by Bromley (1973). Thus

$$\ln \gamma_{\pm} = -2.303\, A\gamma \frac{(\Sigma\, \nu_i Z_i^2) I^{1/2}}{1 + I^{1/2}} + 2.303 \left\{ \frac{(0.06 + 0.6B)}{\left(1 + \frac{1.5I}{\Sigma\, \nu_i Z_i^2}\right)^2} (\Sigma\, \nu_i Z_i^2) I + BI \right\} \tag{4}$$

It can be shown that

$$\ln(\gamma_{\pm})_{\text{stoi}} = (1 - 2\nu') \ln \gamma_{\pm} + \nu'(\ln \gamma_{++} + \ln \gamma_{=}) - p(\nu') \tag{5}$$

where

$$-p(\nu') = (\nu_{++})_{\text{stoi}} \ln \left(1 - \frac{\nu'}{(\nu_{++})_{\text{stoi}}}\right) + (\nu_{=})_{\text{stoi}} \ln \left(1 - \frac{\nu'}{(\nu_{=})_{\text{stoi}}}\right) \tag{6}$$

The stoichiometric osmotic coefficient can be calculated from the thermodynamic relation

$$1 - (\phi)_{\text{stoi}} = -\ln(\gamma_\pm)_{\text{stoi}} + \frac{1}{\Sigma(m_i)_{\text{stoi}}} \int_0^{\Sigma(mi)_{\text{stoi}}} \ln(\gamma_\pm)_{\text{stoi}}\, d\, \Sigma(m_i)_{\text{stoi}} \quad (7)$$

In order to calculate enthalpies and specific heats, the temperature dependence of the parameter B and equilibrium constant K are required. For B, the following equation was used:

$$B = B^* \left(\frac{T-230}{T}\right) + \frac{B_1}{T} + B_2 + B_3 \ln T \quad (8)$$

The variation of the equilibrium constant with temperature is given by

$$\frac{d \ln K}{dT} = \frac{-\Delta H_0}{R} \quad (9)$$

which on integration assuming linear dependence of ΔH_0 on temperature, gives

$$\ln K = -K^* - \frac{K_1}{T} - K_2 \ln \frac{1}{T} \quad (10)$$

B^*, B_1, B_2, B_3 and K^*, K_1, K_2 are constants, values of which are presented in Table 1.

TABLE 1. TEMPERATURE DEPENDENCE OF B AND K IN ION PAIR MODEL

	B		$\ln K$	
Temp. °C	Experimental	Correlated	Experimental	Correlated
40	0.06740	0.06794	5.74	5.21
60	0.07230	0.07139	5.88	5.91
80	0.07121	0.07191	6.01	6.60
100	0.07078	0.07063	7.14	7.26
120	0.06821	0.06818	8.00	7.90

Expression for B:

$$B = \frac{-0.01370\,T}{(T-230)} - \frac{73.4385}{T} + 2.0227 - 0.29037 \ln T$$

Expression for K:

$$\ln K = -106.00 - \frac{5461.26 - 273.16 \times 36.0}{1.9873\,T} - \frac{36.0}{1.9873} \ln \frac{1}{T}$$

Range of validity: 40° to 120°C

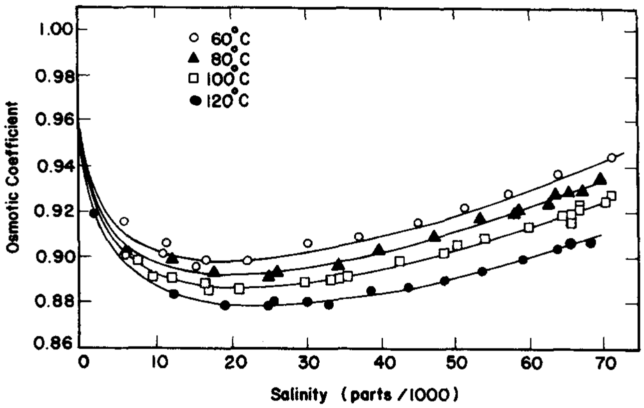

Fig. 1. Stoichiometric osmotic coefficient of sea salt solutions.

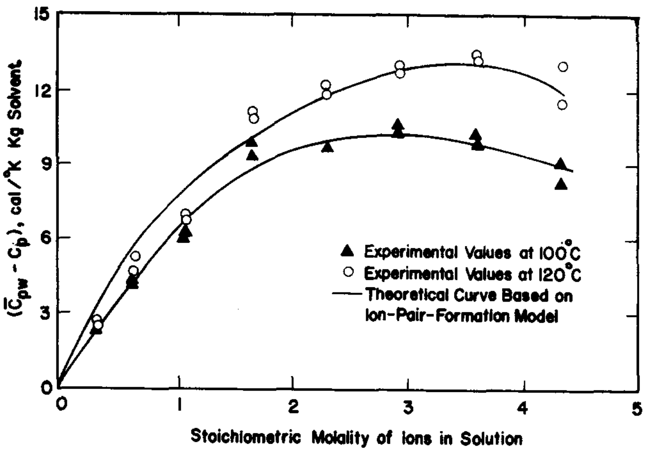

Fig. 2. Comparison of experimental and theoretical heat capacities of sea salt solutions.

C_p: Heat capacity of 1 Kg of pure solvent

$\overline{C}_{pw}$: Heat capacity of 1 Kg of pure solvent

RESULTS

The model was tested in the temperature range 60° to 120°C, and salinity range 0 to 7%. Figure 1 compares the experimental and calculated stoichiometric osmotic coefficients. Figure 2 compares the specific heats of solutions at 100° and 120°C. The present model gives better agreement with the available experimental data than the previous correlations.

NOTATION

A_γ = Debye-Hückel constant
B = parameter in Bromley's correlation
B^*, B_1, B_2, B_3 = constants used for correlating the parameter B with temperature
ΔH_0 = enthalpy of pair formation reaction
I = ionic strength
K = equilibrium constant of pair formation
K^*, K_1, K_2 = constants used for correlating K with temperature
m = molality
p = function defined in text
R = universal gas constant
T = absolute temperature
Z = charge on ion
γ = activity coefficient
ν = ratio of moles of a species to total moles of solute
ϕ = osmotic coefficient

Superscripts

′	refers to pair species

Subscripts

++	refers to equivalent bivalent cation
=	refers to equivalent bivalent anion
±	refers to mean ionic terms
i	refers to ith ionic species
stoi	refers to stoichiometric quantities

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