PVT Properties of Concentrated Aqueous Electrolytes. III. Volume Changes for Mixing the Major Sea Salts at \( I = 1.0 \) and \( I = 3.0 \) at 25 °C

Frank J. Millero, \(^1\) Leslie M. Connaughton, \(^1\) Faina Vinokurova, \(^1\) and Peter V. Chetirkin \(^1\)

Received February 13, 1985; In Final Form September 23, 1985

The densities of mixtures of the six possible combinations of the major sea salts (NaCl, Na\(_2\)SO\(_4\), MgSO\(_4\), and MgCl\(_2\)) were determined at constant ionic strengths of \( I = 1.0 \) and \( I = 3.0 \) at 25 °C. The results are used to determine the volume changes for mixing (\( \Delta V_m \)) the major sea salts. The values of \( \Delta V_m \) were fit to equations of the form \( \Delta V_m = \gamma_2 \gamma_3 l^2 \left[ \nu_0 + \nu_1 (I-2\gamma_3) \right] \) where \( \nu_i \) is the molal ionic strength fraction of solute \( i \), and \( \nu_0 \) and \( \nu_1 \) are parameters related to the interaction of like-charged ions. The cross-square rule was found to hold at both ionic strengths. Density estimates were made without and with the addition of volume of mixing terms to Young's Rule and compared to the experimental values. The densities calculated with the addition of volume of mixing terms gave better estimates, demonstrating that the densities of concentrated brines can be more accurately estimated using \( \Delta V_m \) terms. The equations of Reilly and Wood which include the cross-square rule were used to estimate the densities of the cross mixtures (NaCl-MgSO\(_4\) and MgCl\(_2\)-Na\(_2\)SO\(_4\)). The estimated densities agree with the measured values to within ±30 ppm at \( I = 1.0 \) and ±125 ppm at \( I = 3.0 \).

KEY WORDS: Sea salts; NaCl; Na\(_2\)SO\(_4\); MgSO\(_4\); MgCl\(_2\); volumes of mixing; densities.

1. INTRODUCTION

In order to better understand the physical chemical properties of seawater and other natural waters, it is necessary to understand the ionic interactions occurring in these multicomponent aqueous electrolyte solutions. One of the most important generalizations con-
cerning the behavior of these mixed-salt solutions is that first developed by Young.\(^1\) In the classical work by Young and co-workers\(^{1-4}\) it was demonstrated that the excess thermodynamic properties for reciprocal salt pairs (for example, NaCl-MgSO\(_4\)) of the common ion mixings (NaCl-Na\(_2\)SO\(_4\) + Na\(_2\)SO\(_4\)-MgSO\(_4\) + MgSO\(_4\)-MgCl\(_2\) + MgCl\(_2\)-NaCl) equals the sum of the the excess thermodynamic properties of the uncommon ion mixings (NaCl-MgSO\(_4\) + MgCl\(_2\)-Na\(_2\)SO\(_4\)). This so-called cross-square rule has been shown to hold for a number of electrolyte systems.\(^{5-8}\) This finding is quite useful and has been incorporated into equations used to estimate the properties of mixed electrolyte solutions.\(^{9-16}\) In the past we have been interested in using such equations to estimate the PVT properties of natural waters.\(^{17-21}\) In our recent work\(^{22-28}\) we have extended these studies to higher concentrations and temperatures. In this paper we will report on our studies of the volume of mixing the electrolyte solutions that are the major components of many natural waters. These results should provide data that can be used to make more reliable estimates of the density of concentrated brines.

2. EXPERIMENTAL

Densities of NaCl, Na\(_2\)SO\(_4\), MgSO\(_4\), and MgCl\(_2\) binary solutions and their mixtures were measured at 25 °C using a Picker vibrating flow densimeter\(^{29}\) and a Mettler/Paar vibrating densimeter.\(^{30}\) Both densimeters operate by the same principle: the measurement of the natural vibration frequency of a tube containing a fluid. Since relative densities were desired, the equation used was

\[
\Delta d = d - d_0 = B (\tau^2 - \tau_0^2)
\]

where \(d\) and \(d_0\) are, respectively, the densities of the unknown and reference fluids, \(\tau\) and \(\tau_0\) are, respectively, the periods of the unknown and the reference fluid. The instrument constant \((B)\) is calculated by measuring the period \(\tau\) for two fluids of known density, pure H\(_2\)O (18 M\(\Omega\), ion-exchanged, Millipore Super Q System) and seawater of known conductivity, or pure H\(_2\)O and N\(_2\). The densities of pure H\(_2\)O are taken from Kell,\(^{31}\) the densities of seawater are taken from the International one-atmosphere equation of state of seawater,\(^{32}\) and the densities of N\(_2\) are obtained from the van der Waals' equation.\(^{33}\)

The temperatures of the densimeters were controlled to ±0.005 °C. The temperature was set to ±0.002 °C with a Hewlett-