

**ACTIVITY COEFFICIENT BEHAVIOR IN AQUEOUS BINARY SALT MIXTURES**

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**ABSTRACT**

The activity coefficient behavior of both components in a series of binary salt mixtures containing a common anion has been investigated. It was found that in the case of these mixtures the activity coefficient behavior of both components could be predicted about as well by a simple equation as by the equations of the much more elaborate ion component theory.

With the current upsurge of interest in the physical chemistry of aqueous electrolyte solutions and the consequent availability of new data, especially on electrolyte mixtures, it is now possible not only to correlate trends but also to predict fairly closely thermodynamic behavior in unstudied systems. The purpose of this paper is to compare the activity coefficient behavior of both components in two series of electrolyte mixtures. The first series consists of binary mixtures containing LiCl, NaCl, KCl, RbCl along with CsCl; while the second series consists of NaCl-MgCl, KCl-CaCl, RbCl-SrCl, and CsCl-BaCl mixtures. Two of these mixtures, RbCl-CaCl and RbCl-SrCl, have not been studied experimentally; however, the activity coefficient behavior of both components in each of these mixtures has been predicted and the results will be correlated with the observed behavior in the systems which have been studied. Moreover, the activity coefficients of each component in the mixtures which have been studied have also been computed in two different ways from those of the individual components and these values will be compared with those obtained from the experimental mixture data. All of the activity coefficient values used in the present study were derived from the results of isopiestic measurement on aqueous solutions either of the single salts or of binary mixtures of the salts at 25°.

**METHODS OF CALCULATION**

In treating the isopiestic data both on the single salt solutions and on the salt mixtures the osmotic coefficients derived from the isopiestic measurements were fitted by the method of least squares to equations derived from the "ion component" theory of Scatchard, Rush, and Johnson. For a single salt the expression is

\[
\psi^{\infty} = \frac{1}{(2-n)z^2} \left[ \frac{1}{2-z^2} + \frac{1}{z^2} \right]
\]

(1)

In this equation \( \psi^{\infty} \) is the osmotic coefficient of a salt ca (c = cation, a = anion); \( z_c \) and \( z_a \) are the charges on the cation and anion, respectively; \( m^c \) is the equivalent concentration of the solution; \( S \) is the Debye-Hückel limiting slope (1.17202 at 25°); \( A^c, B^c, A^a, B^a \) are adjustable parameters to be determined by least squares; and \( z_{Ca} \) is given by the expression

\[
\frac{S}{z_{Ca}} = \frac{1}{1 + \frac{S}{A^a B^a}} = 2 \ln \left( 1 + \frac{z^2}{A^c B^c} \right)
\]

(2)

where \( I \) is the ionic strength of the solution. For a mixture of two salts, \( ca \) and \( da \), the equation for the osmotic coefficient of the solution is developed as follows:

\[
\psi^{\infty}_{ca} = \frac{1}{(2-n)z^2} \left[ \frac{z^2}{z^2 + 1} \right] + \frac{1}{(2-n)z^2} \left[ \frac{z^2}{z^2 + 1} \right] + \frac{1}{(2-n)z^2} \left[ \frac{z^2}{z^2 + 1} \right]
\]

(3)

\[
\psi^{\infty}_{da} = \frac{1}{(2-n)z^2} \left[ \frac{z^2}{z^2 + 1} \right] + \frac{1}{(2-n)z^2} \left[ \frac{z^2}{z^2 + 1} \right] + \frac{1}{(2-n)z^2} \left[ \frac{z^2}{z^2 + 1} \right]
\]

Then

\[
\psi_{ca} = \psi^{\infty}_{ca} + \psi^{\infty}_{da} + \psi^{\infty}_{ca} + \psi^{\infty}_{da}
\]

(4)
In the expressions entering into equation (3), all symbols that appear in equation (1) retain their same significance. In equation (3), α represents the equivalent fraction of the respective cations or anions.

In using equation (3) to deduce ionic concentration data on solutions containing two electrolytes (with a common anion or cation) the

concentrations of the two electrolytes (with a common anion or cation) are first evaluated separately. The ionic concentration data on solutions are then

obtained by using the following equations to calculate the activity coefficients φi of each component by least squares using equation (4). These equations

are identical to equations (3) and (4) save that the μ values are the activities of the respective components in the mixtures rather than in the pure solutions.

The concentration of each component can be expressed in terms of its

activity coefficient by

\[ \ln \frac{c_i}{\phi_i} = -x_i \mu_i \]

where \( x_i \) is the equivalent fraction of component \( i \) in the mixture, \( \mu_i \) is the chemical potential of component \( i \) in the mixture, and \( c_i \) is the concentration of component \( i \) in the mixture.

In equation (5), the subscript \( x \) indicates that the activity coefficients \( \phi_i \) are being calculated from the ionic concentration data on solutions containing two electrolytes (with a common anion or cation) which are first evaluated separately.

In the equations entering into equation (6), all symbols that appear in equation (5) retain their same significance.