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ACTIVITY COEFFICIENT BEHAVIOR IN AQUEOUS BINARY SALT MIXTURES[1]

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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,[3] NaCl[4] KCl,[3] or RbCl along with CsCl; while the second series consists of NaCl-MgCl$_2$,[5] KCl-CaCl$_2$,[6] RbCl-SrCl$_2$, and CsCl-BaCl$_2$[7] mixtures. Two of these mixtures, RbCl-CsCl and RbCl-SrCl$_2$ 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[8] 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.[9] For a single salt the expression is

$$(\phi-1)_{ca} = \frac{S}{1/z_c + 1/z_a}(z_a + z_c)\left[\frac{z_{ca}}{A'}\right] + \frac{1}{1/z_c + 1/z_a}\left[B^{(1)}m' + B^{(2)}m'^2 + B^{(3)}m'^3\right] \quad (1)$$

In this equation ϕ is the osmotic coefficient of a salt ca (c $\equiv$ cation, a $\equiv$ anion); z_c and z_a are the charges on the cation and anion, respectively; m' is the equivalent concentration of the solution; S is the Debye-Hückel limiting slope (-1.17202 at 25°); A', $B^{(1)}$, $B^{(2)}$, and $B^{(3)}$ are adjustable parameters to be determined by least squares; and Z_{ca} is given by the expression

$$z_{ca} = \frac{1 + A'\sqrt{I} - \frac{1}{1 + A'\sqrt{I}} - 2\ln(1 + A'\sqrt{I})}{A'^2 I}, \quad (2)$$

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

$$(\phi-1)^{DH} = \frac{S}{x_c/z_c + x_d/z_d + x_a/z_a}\left[x_c x_a (z_c + z_a)\frac{z_{ca}}{A'_{ca}} + x_d x_a(z_d + z_a)\frac{z_{da}}{A'_{da}}\right]$$

$$(\phi-1)^{nI} = \frac{1}{x_c/z_c + x_d/z_d + x_a/z_a}\left[x_c x_a (B_{ca}^{(1)}m' + B_{ca}^{(2)}m'^2 + B_{ca}^{(3)}m'^3) + x_d x_a (B_{da}^{(1)}m' + B_{da}^{(2)}m'^2 + B_{da}^{(3)}m'^3)\right]$$

$$(\phi-1)^{nII} = \frac{1}{x_c/z_c + x_d/z_d + x_a/z_a}\left[x_c x_d x_a (B_{cd}^{(0,1)}m' + B_{cda}^{(0,2)}m'^2 + B_{cda}^{(0,3)}m'^3) + x_c x_d x_a (x_c - x_d)(B_{ccd}^{(1,2)}m'^2 + B_{ccda}^{(1,3)}m'^3) + x_c x_d x_a (x_c - x_d)^2 B_{cccd}^{(2,3)}m'^3\right]$$

Then

$$(\phi-1) = (\phi-1)^{DH} + (\phi-1)^{nI} + (\phi-1)^{nII} \quad (3)$$

In the expressions entering into equation (3) all symbols that also appear in equation (1) retain their same significance, while the x_i represent the equivalent fractions of the respective cations or anions.

In using equation (3) to *fit* osmotic coefficient data on solutions containing two electrolytes (with a common anion) the mixtures parameters A', $B^{(1)}$, $B^{(2)}$, and $B^{(3)}$ for each salt in the mixtures are first evaluated by fitting osmotic coefficient data on solutions of the two salts separately. The resulting values are used in equation (3), so that the only coefficients to be estimated by least squares are $B^{(0,1)}$, $B^{(0,2)}$, $B^{(0,3)}$, $B^{(1,2)}$, $B^{(1,3)}$, and $B^{(2,3)}$. When equation (3) is used to *predict* osmotic coefficient behavior in a mixture these latter six coefficients are ignored and only the $(\emptyset - 1)^{Dff}$ and $(\emptyset - 1)^{nI}$ terms are used. Hence in using equation (3) for predictive purposes only parameters obtained in fitting osmotic coefficient data on the single salt solutions are used.

Activity coefficient expressions both for solutions containing a single salt and for each component in electrolyte mixtures have also been derived from the ion component theory. These expressions contain only parameters that also appear in the corresponding expressions for the osmotic coefficients. For a single salt in solution the activity coefficient is given by

$$\ln \gamma_{ca} = \frac{\sum x_i^2 / \nu \, \emptyset \sqrt{I}}{1 + A' \sqrt{I}} + \frac{1}{1/z_c + 1/z_a} \left[2 B^{(1)} m' + 3/2 \, B^{(2)} m'^2 + 4/3 \, B^{(3)} m'^3 \right] \quad (4)$$

while for a mixture of two salts with a common anion, ca and da, the expression for component ca is

$$\ln \gamma_{ca} = z_c z_a \, \emptyset \sqrt{\frac{X_{ca}}{A'_{ca}} + \frac{1}{x_c z_c + x_d z_d + x_a z_a} \left(x_c (z_c + z_a) \frac{Z_{ca}}{A'_{ca}} \right.}$$

$$\left. + x_d (z_d + z_a) \frac{Z_{da}}{A'_{da}} \right] + \frac{1}{1/z_c + 1/z_a} \left[(x_c + 1) B_{ca}^{(1)} m' + (x_c + \tfrac{1}{2}) B_{ca}^{(2)} m'^2 \right.$$

$$+ (x_c + \tfrac{1}{3}) B_{ca}^{(3)} m'^3 + x_d (B_{da}^{(1)} m' + B_{da}^{(2)} m'^2 + B_{da}^{(3)} m'^3) \right]$$

$$+ \frac{1}{1/z_c + 1/z_a} \left[B_{cd}^{(0,1)} m'_d + \tfrac{1}{2} B_{cdd}^{(1,2)} (m'^2_d - 2 m'_c m'_d) + \tfrac{1}{3} B_{cddd}^{(2,3)} \right.$$

$$(m'^3_d - 4 m_c m'^2_d + 3 m'^2_c m'_d) + \tfrac{1}{2} B_{cda}^{(0,2)} m'_d + \tfrac{1}{3} B_{cda}^{(0,3)} m'_d m'_a$$

$$+ \tfrac{1}{3} B_{cdda}^{(1,3)} (m'^2_d m'_a - 2 m'_c m'_d m'_a) + \tfrac{1}{2} B_{cda}^{(0,2)} m'_c m'_a + \tfrac{1}{3} B_{cda}^{(0,3)} m'_c m'_a$$

$$+ \tfrac{1}{3} B_{ccda}^{(1,3)} (m'^2_c m'_a - m'_c m'_d m'^2_a + \tfrac{1}{3} B_{cda}^{(0,3)} m'_c m'_d m'_a \right] \quad (5)$$

A corresponding expression for $\ln \gamma_{da}$ may be written by exchanging the subscripts ca and da. All terms in equations (4) and (5) that also appear in equations (1) and (3) retain their significance; X is defined as

$$X = \frac{A'^2 I - 2 A' \sqrt{I} + 2 \ln (1 + A' \sqrt{I})}{A'^2 I}, \quad (6)$$

where m' is the total equivalent concentration of the solution. It can be shown that in equation (5) $B^{(1,3)}_{cdda} = - B^{(1,3)}_{ccda}$; hence all the parameters needed to compute the activity coefficient of each component in the mixtures may be evaluated by fitting osmotic coefficient data on the mixtures.

In addition to using the equations derived from the ion component theory, the activity coefficient of each component in the mixtures to be considered will be calculated from those of the pure components using equation (7).

$$\frac{1}{z_c z_a} \ln \gamma_{ca} = \frac{1}{z_c z_a} \ln \gamma^\circ_{ca} + \frac{F_{da}}{2} \left(\frac{1}{z_d z_a} \ln \gamma^\circ_{da} - \frac{1}{z_c z_a} \ln \gamma^\circ_{ca} \right) \quad (7)$$

In this equation the superscript zero indicates the activity coefficient of each respective component in the pure state at the same ionic strength as that for which the activity coefficient of one of the components is being computed in the mixture. The term F_{da} is the ionic strength fraction of component da in a mixture composed of salts ca and da. Equation (7) is con-

sistent with a generalization to unsymmetrical mixtures of the simpler equation

$$\ln \gamma_{ca} = \ln \gamma^\circ_{ca} + \frac{F_{da}}{2} (\ln \gamma^\circ_{da} - \ln \gamma^\circ_{ca}) \quad (8)$$

which holds for symmetrical mixtures and which is similar to an equation given by Harned and Owen.[10] Equation (8) follows directly from Guggenheim's treatment of the theory of specific interaction.

The first step in treating the isopiestic data on the systems to be investigated consisted in fitting the osmotic coefficients of each pure component by least squares using equation (1). This was done in two ways: (1) the value of A' in each case was taken as 1.5 and the parameters $B^{(1)}$, $B^{(2)}$, and $B^{(3)}$ were estimated by least squares; and (2) the value of A' was allowed to vary and A', $B^{(1)}$, $B^{(2)}$, and $B^{(3)}$ were all estimated by least squares. It was found that in the latter case the values of the standard errors of fit were all lower than the values obtained when the value of A' was fixed at 1.5. Hence in all subsequent calculations the results with variable A' were used. The parameters obtained for each salt entering into the mixtures to be considered are summarized in Table I.

The next step in the calculations consisted of fitting the reported osmotic coefficients of the various mixtures using equation (3) and the values of the parameters for each component given in Table I. Then the activity coefficient of each component in the mixtures at total ionic strengths of 1.0 and 3.0 with the ionic strength fraction of each 0.5 was computed using equation (5). These will be referred to as the "fitted" values and are shown plotted as the solid lines in Figures 1 and 2. Values of the activity coefficients under the same conditions were also predicted using only the parameters shown in Table I. These values predicted using the equations of the ion component theory are shown as circles in Figures 1 and 2.

Finally the activity coefficients of each component in the mixtures were computed from the activity coefficient of the pure components using equation (7). The resulting values are shown as triangles in the figures.

TABLE. 1. Values of the Parameters for Equation (1)

Salt	A'	$B^{(1)} \times 10^2$	$B^{(2)} \times 10^2$	$B^{(3)} \times 10^3$
LiCl	1.48213	20.6250	1.48505	0.0457623
NaCl	1.46645	4.16487	1.99370	−1.23737
KCl	1.27229	.117440	1.13968	− .752042
RbCl	1.10788	.723839	.850918	− .617635
CsCl	0.928134	−.293560	1.55263	−2.55128
MgCl₂	1.73021	11.3647	4.45536	−2.88254
CaCl₂	1.67010	8.40142	3.89299	−2.96880
SrCl₂	1.64768	6.36679	3.54828	−2.70791
BaCl₂	1.66228	.150021	.480582	− .211564

RESULTS OF THE CALCULATIONS

Consider the mixtures containing CsCl and each of the other alkali metal chlorides as shown in Figure 1. The first three mixtures starting at the left have been studied isopiestically, while to our knowledge the RbCl-CsCl mixture has not been studied experimentally. Note that at both total ionic strengths the log γ^{CsCl} is nearly constant, while that of the other salt decreases in going from LiCl-CsCl to RbCl-CsCl. At I = 1.0 both methods of predicting give comparable and very good results; at I = 3.0 both methods of predicting give relatively poor results for LiCl-CsCl mixtures, somewhat better results for NaCl-CsCl, and excellent for KCl-CsCl mixtures. At both total ionic strengths the predic-

tions on RbCl-CsCl mixtures are consistent with the measured values on the other systems and are probably very close to the actual values.
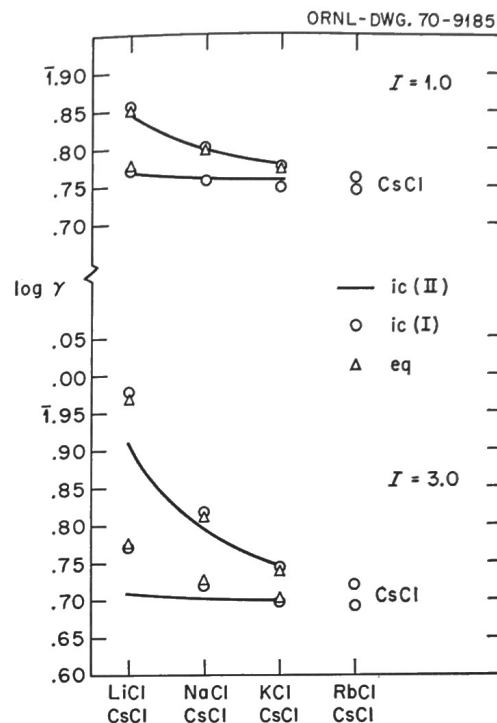

Figure 1. Activity coefficient behavior in binary mixtures containing LiCl, NaCl, KCl and RbCl along with CsCl at total ionic strengths 1.0 and 3.0.

All of the systems depicted in Figure 2 except RbCl-SrCl₂ have been studied experimentally. Observe that there is very little difference in the values predicted by the two methods at I = 1.0. It is interesting to note that equation (7) seems to predict a more consistent value of log γ^{SrCl_2} at I = 3.0 than does the ion component treatment. The fact that the log γ values predicted for the RbCl-SrCl₂ system seem to be high at I = 3.0 suggests that these two salts should be reinvestigated. This statement is made in consideration of the fact that when the old values[8] of the activity of CsCl were used in predicting the activity coefficient behavior in CsCl-BaCl₂ mixtures[7] by either method the log γ values were too high, while when Lindenbaum's newer values[7] for CsCl were used both the predicted and observed values agreed closely.

From the results of these studies it appears that the simple equation (7) predicts the activity coefficient values of both components in binary mixtures of salts with a common anion about as well as does the much more elaborate ion component method. Further calcu-

lations will be necessary to determine whether this is true in more complicated mixtures as well.

The authors wish to thank Dr. R. W. Stoughton for suggesting the inclusion of the charge factors in Equation (7).
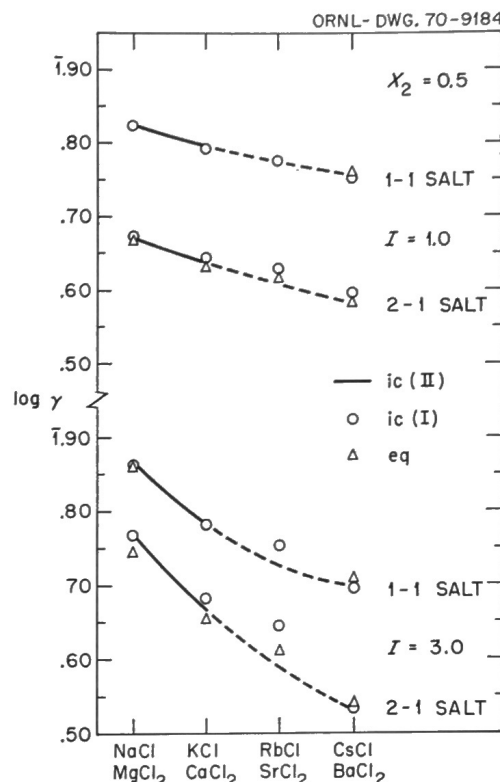

Figure 2. Activity coefficient behavior in NaCl-MgCl₂, KCl-CaCl₂, RbCl-SrCl₂ and CsCl-BaCl₂ mixtures at ionic strengths 1.0 and 3.0.

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