

# A REEVALUATION OF THE ACTIVITY COEFFICIENTS IN THE SYSTEM NaCl-KCl-H<sub>2</sub>O\*

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## INTRODUCTION

In the study of aqueous solutions of two electrolytes, isopiestic vapor pressure measurements provide valuable information about the water activity of the solution. This water activity can also be expressed in terms of the osmotic coefficient of the solution.

$$\bar{w}_O \phi (v_{A-A}^m + v_{B-B}^m) = - \ln \bar{a}_w \quad (1)$$

But the activity coefficients of the two electrolytes are not given directly by vapor pressure measurements. McKay and Perring<sup>1</sup> have obtained an equation which is particularly suited to the treatment of isopiestic data but, while it is elegant in principle, it involves an integration from zero concentration upwards. It is in this region of low concentration that isopiestic data are least reliable and, therefore, there is always some doubt about the behavior of this integral term in the region of low concentration. Thus, calculations even at high concentrations are affected.

These difficulties were overcome<sup>2,3</sup> for solutions of two nonelectrolytes (or one electrolyte + one nonelectrolyte) by means of the function

$$\Delta = \phi (v_{A-A}^m + v_{B-B}^m) - v_{A-A}^m \phi_A^O - v_{B-B}^m \phi_B^O \quad (2)$$

where  $\phi_A^O$  is the osmotic coefficient of a solution containing only solute A at a concentration,  $\bar{m}_A$ , identical with that of solute A in the mixed solution.

Similarly,  $\phi_B^O$  is the osmotic coefficient of a solution containing only solute B at a concentration,  $\bar{m}_B$ , identical with that of solute B in the mixed solution. For a nonelectrolyte,  $v = 1$ . It was found that  $\Delta / (\bar{m}_A \bar{m}_B)$

was small and could be represented by a power series in  $\bar{m}_A$  and  $\bar{m}_B$ . It was also shown that the activity coefficients could be calculated easily, once the parameters of the power series were known.

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\*\*\* Symbols are defined at the end of the paper.

It is worthwhile to consider if this method could be used for a solution of two electrolytes. Consider the system: sodium chloride (A) — potassium chloride (B).<sup>4</sup> Taking one particular result, it was found that a solution of 4.0043  $\bar{m}$  sodium chloride (with no potassium chloride) had the same vapor pressure as a solution containing 2.1700  $\bar{m}$  sodium chloride and 2.1391  $\bar{m}$  potassium chloride. The osmotic coefficient of a solution of 4.0043  $\bar{m}$  sodium chloride is 1.1161,<sup>5</sup> and therefore the first term on the right of Equation (2) is 8.9384. But the osmotic coefficient of a solution of 2.1700  $\bar{m}$  sodium chloride is 0.9931<sup>5</sup> and that of a solution of 2.1391  $\bar{m}$  potassium chloride is 0.9155,<sup>5</sup> so that the last two terms on the right of Equation (2) are 4.3101 and 3.9167, respectively, and  $\Delta = 0.7116$ . This is a large value of  $\Delta$  and, while it might be expressed as a power series in  $\bar{m}_A$  and  $\bar{m}_B$ , it is not particularly well suited to this purpose.

We now anticipate a result to be described later.

Suppose  $\phi_A^O$  and  $\phi_B^O$  are given their values, not at the molalities of each salt in the mixed solution, but at the total molality of the mixed solution, 4.3091

$\bar{m}$  in the above example. Thus  $\phi_A^O = 1.1388$  and  $\phi_B^O = 0.9739$ ,  $\Delta = -0.1705$ .

$\Delta$  is now much smaller and should be more easily expressed as a power series.

An even simpler deviation function would be

$$\Delta = 2 \phi - 2 \bar{y}_A \phi_A^O - 2 \bar{y}_B \phi_B^O \quad (3)$$

again giving  $\phi_A^O$  and  $\phi_B^O$  their values at a molality identical with that of the mixed solution. For the example quoted above,  $\Delta = -0.0396$ . Figure 1 shows values of  $\Delta$  for a number of mixed sodium chloride-potassium chloride solutions, all of which were in vapor phase equilibrium with an approximately 4  $\bar{m}$  sodium chloride solution. Inspection of this figure suggests that, to a first approximation, we can write

$$\Delta = \bar{a} \bar{y}_A \bar{y}_B \quad (4)$$

where  $\bar{a}$  is a function to be evaluated.

The difficulties with the integration in the McKay Perring method may also be avoided by a procedure suggested by Scatchard.<sup>6,7</sup> In this case, an equation for the excess free energy is given. When this equation

is differentiated with respect to the amount of solvent, an expression involving the osmotic coefficient is obtained; when the differentiation is with respect to the number of moles of component J, an expression involving the activity coefficient  $\gamma_J$  is obtained. We have applied this procedure to the data of Robinson<sup>4</sup> on the three-component system NaCl-KCl-H<sub>2</sub>O and compared these results with those he obtained by the McKay-Perring method.

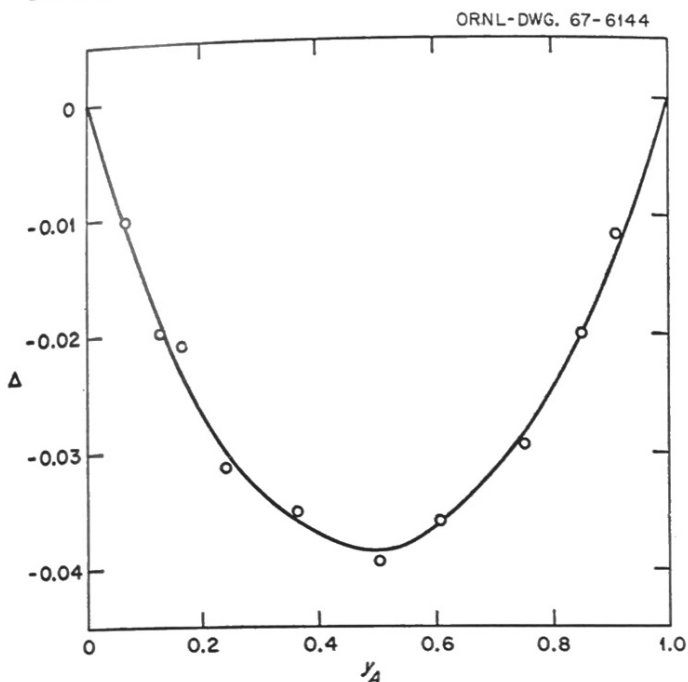


Figure 1

$\Delta = 2\phi - 2y_A \phi_A^\circ - 2y_B \phi_B^\circ$ , A IS SODIUM CHLORIDE AND B IS POTASSIUM CHLORIDE

METHOD

We turn now to the equations developed by Scatchard<sup>6</sup> and applied by him to various data including the reciprocal salt pair K<sup>+</sup>, Li<sup>+</sup>-NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>. We limit ourselves to a consideration of solutions containing two electrolytes each of the 1:1 charge type. In this case, Scatchard's equation for the osmotic coefficient of the solution of two electrolytes can be written

$$2(\phi - 1) = \alpha_A y_A + \alpha_B y_B + \beta_{AB}^{(0)} y_A y_B + \beta_{AB}^{(1)} y_A y_B (y_A - y_B) \quad (5)$$

where the contributions of the single salts,  $\alpha_A$  and  $\alpha_B$ , are expressed as a Debye-Huckel term plus a polynomial in  $m$

$$\alpha_J = \frac{(2)(-1.17082)}{\rho_J^3 m} \left[ 1 + \rho_J m^{\frac{1}{2}} - \frac{1}{1 + \rho_J m^{\frac{1}{2}}} - 2 \ln(1 + \rho_J m^{\frac{1}{2}}) \right] \quad (6)$$

$$+ \underline{a}_J^{(1)} m + \underline{a}_J^{(2)} m^2 + \underline{a}_J^{(3)} m^3 + \underline{a}_J^{(4)} m^4 \cdot$$

Since the Debye-Huckel contribution is separated into  $\alpha_A$  and  $\alpha_B$ , it is possible to use different values of the ion-size parameter,  $\rho$ , for the two components of the

mixture. In Equation (5),  $\Phi$  is known from measurements of solutions containing both electrolytes A and B and  $\alpha_A$  and  $\alpha_B$  are known from measurements of solutions of the pure salts. The next step is to express

$\beta_{AB}^{(0)}$  and  $\beta_{AB}^{(1)}$  as polynomials in  $m$

$$\beta_{AB}^{(0)} = \underline{b}_{AB}^{(0,1)} m + \underline{b}_{AB}^{(0,2)} m^2 + \underline{b}_{AB}^{(0,3)} m^3 \quad (7)$$

$$\beta_{AB}^{(1)} = \underline{b}_{AB}^{(1,2)} m^2 + \underline{b}_{AB}^{(1,3)} m^3 \quad (8)$$

We now consider the activity coefficients. From Equation (5), we can derive equations for the activity coefficients of the separate components A and B

$$2 \ln \gamma_A = \underline{A}_A + \alpha_A + (\alpha_B - \alpha_A) y_B + \beta_{AB}^{(0)} y_B + (\underline{B}_{AB}^{(0)} - \beta_{AB}^{(0)}) y_B^2 + \beta_{AB}^{(1)} y_B + 3(\underline{B}_{AB}^{(1)} - \beta_{AB}^{(1)}) y_B^2 - 2(2\underline{B}_{AB}^{(1)} - \beta_{AB}^{(1)}) y_B^3 \quad (9)$$

$$2 \ln \gamma_B = \underline{A}_B + \alpha_B + (\alpha_A - \alpha_B) y_A + \beta_{AB}^{(0)} y_A + (\underline{B}_{AB}^{(0)} - \beta_{AB}^{(0)}) y_A^2 - \beta_{AB}^{(1)} y_A - 3(\underline{B}_{AB}^{(1)} - \beta_{AB}^{(1)}) y_A^2 + 2(2\underline{B}_{AB}^{(1)} - \beta_{AB}^{(1)}) y_A^3 \quad (10)$$

The  $\underline{A}$  and  $\underline{B}$  quantities are defined by

$$\alpha = m \frac{\partial \underline{A}}{\partial m} \quad \text{and} \quad \beta = m \frac{\partial \underline{B}}{\partial m},$$

thus,

$$(\underline{A}_J + \alpha_J) = \frac{(2)(-1.17082) m^{\frac{1}{2}}}{1 + \rho_J m^{\frac{1}{2}}} + 2 \underline{a}_J^{(1)} m + \frac{3}{2} \underline{a}_J^{(2)} m^2 + \frac{4}{3} \underline{a}_J^{(3)} m^3 + \frac{5}{4} \underline{a}_J^{(4)} m^4 \quad (11)$$

$$\underline{B}_{AB}^{(0)} = \underline{b}_{AB}^{(0,1)} m + \frac{1}{2} \underline{b}_{AB}^{(0,2)} m^2 + \frac{1}{3} \underline{b}_{AB}^{(0,3)} m^3 \quad (12)$$

$$\underline{B}_{AB}^{(1)} = \frac{1}{2} \underline{b}_{AB}^{(1,2)} m^2 + \frac{1}{3} \underline{b}_{AB}^{(1,3)} m^3 \quad (13)$$

Here again, the contributions of the limiting two-component systems are separate, and the ion-size parameters need not be the same. If only those terms containing  $\alpha$  or  $\underline{A}$  are considered (the first three terms in Equations (9) and (10)), Equations (9) and (10) provide a means of estimating the activity coefficients

for the mixtures from the limiting two-component systems.

### RESULTS

The coefficients of Equation (6) were evaluated by a least squares fit to the data given by Robinson and Stokes.<sup>5</sup> The coefficients obtained are as follows:

	$p$	(1) $\underline{a}$	(2) $\underline{a}$	(3) $\underline{a}$	(4) $\underline{a}$
NaCl	1.5	0.03684	0.02108	-0.001304	0
KCl	1.5	-0.06408	0.05244	-0.01124	0.000918

By the method of least squares the data of Robinson for the three-component system NaCl-KCl-H<sub>2</sub>O<sup>4</sup> were then used to obtain values for the  $\beta$ -coefficients of Equation (5) as given by Equations (7) and (8). We

find that only the coefficients  $\underline{b}_{AB}^{(0,1)}$  and  $\underline{b}_{AB}^{(0,2)}$

are needed; inclusion of additional coefficients did not improve the fit to the data. The values obtained are

$$\underline{b}_{AB}^{(0,1)} = -0.0253$$

and

$$\underline{b}_{AB}^{(0,2)} = -0.00299;$$

these result in a standard deviation of 0.0008 in  $\phi$ .

For convenience, we may write

$$2 \ln \gamma_J^0 = \underline{A}_J + \alpha_J. \quad (14)$$

Using this substitution and the values of the coefficients given above, Equations (9) and (10) become

$$\log \gamma_A / \gamma_A^0 = (-0.02741 \underline{m} + 0.006160 \underline{m}^2 - 0.002158 \underline{m}^3 + 0.0001993 \underline{m}^4) \underline{y}_B + 0.000325 \underline{m}^2 \underline{y}_B^2 \quad (15)$$

$$\log \gamma_B / \gamma_B^0 = (0.01642 \underline{m} - 0.007459 \underline{m}^2 + 0.002158 \underline{m}^3 - 0.0001993 \underline{m}^4) \underline{y}_A + 0.000325 \underline{m}^2 \underline{y}_A^2 \quad (16)$$

where A is sodium chloride and B is potassium chloride.

TABLE I  
ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE (A) AND POTASSIUM CHLORIDE (B)  
IN MIXED SOLUTION CALCULATED BY TWO METHODS

		$\log \gamma_A / \gamma_A^0$					
$y_B$	B	$m = 1$		$m = 3$		$m = 5$	
		0.2	-0.0046 <sup>a</sup>	-0.0047 <sup>b</sup>	-0.0137 <sup>a</sup>	-0.0139 <sup>b</sup>	-0.0253 <sup>a</sup>
.4	- .0092	- .0093	- .0275	- .0275	- .0500	- .0500	
.6	- .0138	- .0139	- .0403	- .0407	- .0740	- .0735	
.8	- .0184	- .0185	- .0532	- .0535	- .0973	- .0960	
1.0	- .0229	- .0230	- .0660	- .0660	- .1200	- .1175	

		$\log \gamma_B / \gamma_B^0$					
$y_A$	A	$m = 1$		$m = 3$		$m = 5$	
		0.2	0.0022 <sup>c</sup>	0.0019 <sup>b</sup>	0.0050 <sup>c</sup>	0.0050 <sup>b</sup>	0.0085 <sup>c</sup>
.4	.0044	.0038	.0102	.0101	.0176	.0196	
.6	.0067	.0057	.0156	.0151	.0274	.0294	
.8	.0090	.0076	.0213	.0202	.0378	.0392	
1.0	.0113	.0095	.0272	.0252	.0489	.0490	

a. Calculated using Equation (15).

b. Calculated by the method in Reference (4).

c. Calculated using Equation (16).