

PROBLEMS ENCOUNTERED IN DERIVING ACTIVITY COEFFICIENT VALUES FROM DATA ON MIXED ELECTROLYTE SYSTEMS*

M. H. LIETZKE and R. W. STOUGHTON
 Oak Ridge National Laboratory
 Oak Ridge, Tennessee 37830

Difficulties which may be encountered in deriving activity coefficient values from data on mixed electrolyte systems are discussed, the most serious being statistical correlation between the parameters of the mathematical expression used in fitting the data. It is suggested that when correlation is a problem, predicted values of the activity coefficient of each component in the mixture may be preferable to values calculated from the parameters estimated by fitting the experimental data in cases where only part of the parameters are used in calculating the activity coefficient values.

INTRODUCTION

Recent developments in fields such as geochemistry, waste disposal, oceanography, and desalination have made it necessary to have information on the thermodynamic properties of aqueous solutions containing more than one electrolyte. Such properties might include the osmotic coefficient of the solution or the activity coefficient of each component in the solution. Depending upon the property desired, difficulties may be encountered, however, in deriving numerical values from experimental data. The purpose of this paper is to identify the source of the difficulties and to suggest ways of circumventing the problem.

MATERIALS AND METHODS

Osmotic coefficients. The osmotic coefficient of a mixed electrolyte system is usually measured by the isopiestic technique (Robinson and Stokes, 1965). A series of solutions of varying total ionic strength and composition is equilibrated isopiastically with a reference solution (usually NaCl or KCl) whose osmotic coefficient is known as a function of concentration from absolute vapor pressure measurements. From the isopiestic ratios so obtained the osmotic coefficients of the mixed electrolyte solutions are readily calculated. Finally, the osmotic coefficient values may be fitted by the method of least squares on a high speed computer to an equation expressing the osmotic coefficient as a function of total ionic strength, composition, and a number of parameters specifying the explicit dependency of the osmotic coefficient on these independent variables. This equation may then be solved to give the osmotic coefficient of any arbitrary solution (within the range of the original data) or the parameters of the equation may be used in appropriate expressions to calculate the activity coefficient of each component (electrolyte) in the mixture.

Whenever experimental data, such as osmotic coefficients, are fitted by least squares to a mathematical equation to ob-

tain estimates of the parameters (constants) in the equation, it is found that the parameters are to some degree correlated. The degree of correlation (which gives a measure of how well the individual parameters are determined) may vary in specific instances from very slight to very great. There is no way to predict *a priori* the extent of correlation to be expected when a given equation is fitted to a given set of experimental data. The same equation when fitted to two different sets of data may yield estimates of the parameters that are correlated to a different extent although both sets of data may be very well represented by the equation when the appropriate set of parameters is used.

Several models (Scatchard, 1961; Reilly et al., 1971) have been formulated that express the osmotic coefficient of a mixed electrolyte system as a function of total ionic strength and composition. The assumptions underlying the several models lead to varying explicit functional dependencies of the osmotic coefficient upon the independent variables (total ionic strength and composition). However, all these models can be used about equally well to fit osmotic coefficient data on electrolyte mixtures. In each case the parameters estimated by least squares from the osmotic coefficient data may be used to calculate the activity coefficient of each component in the mixtures. The important point here is that *all* the parameters obtained in the original fit are used in calculating the derived quantities (activity coefficients). Hence the degree of correlation between the parameters in a given model is not of much consequence. In support of this last statement, it can be shown not only that measured values of the osmotic coefficients of representative electrolyte mixtures are consistent with values predicted from single electrolyte osmotic coefficient data (Lietzke and Stoughton, in press), but that values of the activity coefficients of the components of the mixtures calculated using the parameters estimated by fitting the osmotic coefficients are also consistent with values predicted for these components from single electrolyte activity coefficient data (Lietzke and Stoughton, 1972). For example, consider aqueous KCl-CaCl₂ mixtures. When experimental osmotic coefficients for this system (Robinson and Covington, 1968) are fitted to an equation suggested by Scatchard (1961) and the equation solved at I = 1.0 and 2.0 for varying fractions X₂ of CaCl₂ in the mixtures, then the values shown in the first part of Table I under the heading $\phi_{(t)}$ are obtained. Values predicted for the mixtures from the osmotic coefficients of pure KCl and pure CaCl₂ solutions (Lietzke and Stoughton, in press) are shown under the column headed $\phi_{(p)}$. Note that in all cases the predicted values are within less than one percent of the fitted observed values. The logarithms of the activity coefficients of both the KCl and the CaCl₂ in the mixtures are shown in the second part of Table I. The values under the headings KCl_(t) and CaCl_{2(t)} represent values calculated from the parameters obtained by fitting the osmotic coefficients, while the values under the headings KCl_(p) and CaCl_{2(p)} have been predicted by a simple equation which neglects short range ionic interactions in the mixtures (Lietzke and Stoughton, in press). Again the agreement and consistency of both sets of values are very good. Hence the fact that the parameters obtained in the original fit of the osmotic coefficient values may have been strongly correlated does not severely affect the values of the activity coefficients.

TABLE I: Osmotic and activity coefficient values for KCl-CaCl₂ mixtures

1. Osmotic Coefficients (ϕ)					
I	X ₂	$\phi_{(t)}$	$\phi_{(p)}$		
1.0	0.25	0.902	0.895		
1.0	.50	.900	.892		
1.0	.75	.893	.888		
2.0	.25	.921	.917		
2.0	.50	.932	.926		
2.0	.75	.944	.938		

2. Activity Coefficients (γ)					
I	X ₂	KCl _(t)	KCl _(p)	CaCl _{2(t)}	CaCl _{2(p)}
1.0	0.25	0.797	0.787	0.636	0.620
1.0	.50	.803	.792	.639	.632
1.0	.75	.809	.798	.643	.644
2.0	.25	.775	.766	.630	.606
2.0	.50	.786	.776	.636	.625
2.0	.75	.797	.785	.645	.643

form where E° is the standard potential of the Ag, AgX electrode; m_±, m_±, and m_± are the molalities of HX, MX, and NX₂, respectively; T is the absolute temperature; R is the gas constant; F is the Faraday; and γ_{\pm} is the mean ionic activity coefficient of the HX. If the "neutral electrolyte" treatment (Scatchard, 1961) is used to derive expressions for the activity coefficients of each component in the mixture, then

$$\log \gamma_{\pm} = \log \gamma_{\pm}^{\circ} - \frac{S\sqrt{I}}{1 + 1.5\sqrt{I}}$$

where the excess term may be expressed as a linear combination coefficients:

In equations (1), (2), and (3), γ_{\pm} , γ_{\pm} and γ_{\pm} refer to the activity coefficients of HX, MX, and NX₂, respectively; S' is the appropriate Debye-Hückel limiting slope; I is the ionic strength of the solution (I = m_± + m_± + 3m_±); and 1.5 is used in each case as the denominator parameter in the Debye-Hückel expressions. In equations (1a), (2a), and (3a) the B₁₁ and C₁₁₂ represent interaction parameters to be determined from experimental data, while X₂, X₂ and X₂ refer to the ionic strength fractions of the designated components in the mixture. The parameters in equation (1a),

$$\log \gamma_{\pm} = 2I [B_{22} + (B_{22} - B_{22}) X_2 + (B_{21}/3 - B_{22}) X_1] + 3I^2 [C_{222} + 2(C_{222} - C_{222}) X_2 + 2(C_{221}/3 - C_{222}) X_1] + 3I^3 [2(C_{222} - C_{222} + C_{221}/3 - C_{221}/3) X_2 X_1 + C_{222} + (C_{222} - 2C_{222}) X_2^2 + (C_{222} + C_{221}/9 - 2/3 C_{222}) X_1^2]; \quad (1a)$$

$$\log \gamma_{\pm} = \log \gamma_{\pm}^{\circ} - (S' \sqrt{I}) / (1 + 1.5 \sqrt{I}) \quad (2)$$

where

$$\log \gamma_{\pm}^{\circ} = 2I [B_{22} + (B_{22} - B_{22}) X_2 + (B_{21}/3 - B_{22}) X_1] + 3I^2 [C_{222} + 2(C_{222} - C_{222}) X_2 + 2(C_{221}/3 - C_{222}) X_1] + (C_{222} + C_{221}/9 - 2/3 C_{222}) X_2^2 + (C_{222} - C_{222} + C_{221}/3) X_1 X_2]; \quad (2a)$$

and

$$\log \gamma_{\pm} = \log \gamma_{\pm}^{\circ} - (S' \sqrt{I}) / (1 + 1.5 \sqrt{I}) \quad (3)$$

where

$$\log \gamma_{\pm}^{\circ} = 4/3 I [B_{11}/3 + B_{11} - B_{11}/3] X_2 + (B_{21} - B_{11}/3) X_2 + 2I^2 [C_{211}/9 + 2(C_{211}/3 - C_{211}/9) X_2 + 2(C_{211}/3 - C_{211}/9) X_1 + (C_{222} - 2/3 C_{222} + C_{221}/9) X_2^2 + (C_{221} - 2/3 C_{221} + C_{211}/9) X_2 X_1 + 2(C_{221} - C_{211}/3 - C_{211}/9) X_1 X_2]; \quad (3a)$$

Activity Coefficients. In the preceding section it was shown that good estimates of the activity coefficient of each component in an aqueous electrolyte mixture could be calculated from the parameters obtained by fitting osmotic coefficient data on the mixture since all the parameters estimated in the fit were used in calculating the activity coefficient values. Many experimental techniques, however, e.g., electromotive force measurements, yield not osmotic coefficients but activity coefficients. For example, by the use of a hydrogen electrode and a silver, silver chloride reference electrode one can measure the activity of HCl in an aqueous solution containing HCl and one or more chloride salts. Since the concentration of the HCl in the solution can be measured by analysis, the activity coefficient of the HCl may then be computed. It is impossible, however, to compute the activity coefficient of the salt or salts in the mixture without additional information on either the pure single salt solution or on the two-salt solution. Either osmotic or activity coefficient data on these latter solutions must be used in estimating the additional parameters needed in order to calculate the activity coefficients of the salts in the mixtures containing the acid, whose activity coefficient is directly measured. It is at this point that difficulties arise: in order to calculate the salt activity coefficients it is necessary to use members taken from two different sets of correlated parameters. If the extent of correlation between the members of one or both sets is high, then poor estimates of the salt activity coefficients may well be obtained.

To illustrate the above points, a specific example will now be given. Consider an aqueous electrolyte mixture containing a halogen acid HX, a monovalent salt of this acid MX, and a divalent salt of the acid NX₂. Let the subscript ₂ refer to HX, ₁ to MX, and ₂ to NX₂. Suppose emf measurements are made of the cell



The emf of this cell E is given by the Nernst equation in the

$$E = E^{\circ} - (RT/F) \ln [m_2(m_1 + m_2 + 2m_2)] - (2RT/F) \ln \gamma_{\pm}$$

namely B₂₂, B₂₁, B₂₁, C₂₂₂, C₂₂₁, C₂₂₁, C₂₂₁, C₂₂₁ may all be estimated by least squares by fitting values of log γ_{\pm} computed using the Nernst equation for each experimental emf value. Equation (1a) may then be solved at any total ionic strength with specific

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values of X_2 , X_3 , and X_4 to give values of $\log \gamma_2$ in the corresponding mixture. Even though the various B_{ij} and C_{ij} parameters in this equation may be correlated, good estimates of $\log \gamma_2$ are invariably obtained since all the parameters are used in the calculation.

Examination of equations (2a) and (3a) reveals the fact that there are seven parameters needed to calculate values of $\log \gamma_2$ and $\log \gamma_1$ in the mixtures that cannot be obtained from emf measurements of the HX activity in the mixtures. These are the coefficients B_{23} , B_{31} , B_{11} , C_{233} , C_{331} , C_{311} , and C_{111} . In order to evaluate these quantities, an independent study (usually isopiestic) must be made of aqueous MX, NX₂ solutions. From these measurements estimates of the above seven parameters may be derived, and in general, these estimates will again be correlated.

Equations (2a) and (3a) each contain four parameters (only one the same) from the set obtained by fitting the $\log \gamma_2$ values and five parameters (three the same) derived from data on the MX, NX₂ solutions. Hence the extent to which the parameters are individually well determined (i.e., not strongly correlated with others in the set from which they were taken) will determine whether or not the calculated values of $\log \gamma_2$ and $\log \gamma_1$ are reasonable estimates. A possible criterion as to whether or not they are reasonable estimates might be the agreement between these $\log \gamma$ values and $\log \gamma$ values predicted by the simple equation presented by Lietzke and Stoughton (1972), or $\log \gamma$ values predicted by a more elaborate treatment such as that of Scatchard, Rush, and Johnson (1970).

The foregoing treatment has been used in computing activity coefficient values for each component in a number of three electrolyte mixtures, including the HCl-NaCl-MgCl₂ (Lietzke and Herdtklotz, 1971) and the HBr-NaBr-ZnBr₂ (Lietzke and Danford, 1973) systems. In each case the activity of the acid was measured by the emf technique, while the salt pair was investigated isopiastically.

RESULTS

HCl-NaCl-MgCl₂ mixtures. In this system correlation between the estimates of the parameters obtained both in the fit of the HCl activity coefficients and in the fit of the osmotic coefficients of the salt solutions was relatively low. Except for the B_{22} - C_{222} correlation (correlation coefficient = 0.794) all other correlation coefficients (computed from the elements of the least squares inverse matrix) lay between -0.3 and +0.3. As shown in Table 2 the agreement between the logarithms of the salt activity coefficient values computed from the parameters obtained in the least squares fits and values predicted by the simple equation presented by Lietzke and Stoughton (1972) is very satisfactory (within a few percent).

HBr-NaBr-ZnBr₂ mixtures. In this system correlation between the estimates of the parameters obtained in both least squares fits were much higher than in the HCl-NaCl-MgCl₂ system. The correlation coefficient

TABLE 2: Activity coefficient values in HCl-NaCl-MgCl₂ mixtures

I	$\log \gamma + 1$								
	X_2	X_3	X_4	HCl _(f)	HCl _(p)	NaCl _(f)	NaCl _(p)	MgCl _{2(f)}	MgCl _{2(p)}
1.0	0.75	0.125	0.125	0.909	0.898	0.877	0.853	0.732	0.724
1.0	.50	.250	.250	.901	.888	.861	.843	.709	.704
1.0	.25	.375	.375	.892	.878	.846	.833	.689	.683

for the B_{22} - C_{222} correlation was 0.999, while the remaining coefficients lay between -0.65 and +0.65. As can be seen in Table 3 the agreement between the predicted and fitted values of the logarithms of the salt activity coefficients is very poor even though the total ionic strength of the solution is only 0.3, compared to 1.0 in the former system. In contrast, the logarithms of the salt activity coefficients in the NaBr-ZnBr₂ system alone, computed from parameters obtained by fitting osmotic coefficients for the solutions, agreed very closely with values predicted by the simple equation. This was as expected, since all the parameters from the osmotic coefficient fit were used in the calculation of the activity coefficient values of both salts in the mixture.

Other three-electrolyte systems that have been investigated by the foregoing technique include HCl-KCl-CaCl₂ (Lietzke and Daugherty, 1972), HCl-CsCl-BaCl₂ (Lietzke et al., 1969), HCl-NaCl-LaCl₃ (Lietzke and Danford, 1972), and HCl-MgCl₂-CaCl₂ (Lietzke and Danford, 1973) mixtures. In no case was the problem of correlation as severe in these systems as in the HBr-NaBr-ZnBr₂ system, although moderate disagreement was observed between predicted and fitted values of the activity coefficients of the BaCl₂ and the LaCl₃ in their respective mixtures. In all two-electrolyte and three-electrolyte systems that have been investigated by the foregoing techniques, the best agreement between $\log \gamma$ values calculated from the parameters of the fits and predicted $\log \gamma$ values was observed with mixtures involving smaller cations.

DISCUSSION

The problems discussed in the foregoing sections are by no means specific to the particular models used in the examples. They are encountered whenever members of two separate sets of correlated parameters are combined in the calculation of some desired quantity. In the case of activity coefficients, where several different treatments may be used in fitting the data, there is the further problem (beyond the problem of correlation) that the values are sensitive to the method of calculation used. For example, values of the activity coefficient of NaCl in HCl-NaCl mixtures may differ by as much as one percent or more, depending upon whether they were obtained by cross-differentiation (Bjerrum, 1923) or by application of the "neutral electrolyte" treatment (Scatchard, 1961) to HCl-NaCl mixture data (Lietzke and Stoughton, 1964). This makes it

TABLE 3: Activity coefficient values in HBr-NaBr-ZnBr₂ mixtures

I	X_2	X_3	X_4	HBr _(f)	HBr _(p)	NaBr _(f)	NaBr _(p)	ZnBr _{2(f)}	ZnBr _{2(p)}
0.3	0.75	0.125	0.125	0.889	0.887	1.103	0.871	0.272	0.773
.3	.50	.250	.250	.885	.885	1.045	.869	.394	.768
.3	.25	.375	.375	.881	.883	0.968	.866	.551	.764

impossible to state, for example, whether the activity coefficient of NaCl at 10°C in a 50:50 % mixture at I = 1.0 is 0.700 or 0.709 (Lietzke and Stoughton, 1964). It has also been shown (Lietzke and Stoughton, 1972) that similar results are obtained when the "neutral electrolyte" treatment and an ion-component treatment (Scatchard et al., 1970) are applied to the same set of mixture data by the method of least squares. The differences may partly result from a difference in weighting when attention is focussed on the ions as components or on the electrolytes themselves. In addition any approximations made in the derivation of the various models may manifest themselves differently and result in slight differences in the predicted values of the activity coefficients of the components of a mixture.

SUMMARY

In view of the difficulties associated with treating thermodynamic data on mixed electrolyte systems, the following recommendations are made. Whenever possible, osmotic coefficient data should be used for calculating the activity coefficient values of each component in mixed electrolyte systems, because, as shown above, all the parameters obtained in the fit of the osmotic coefficients are used in calculating the activity coefficients, and the problem of statistical correlation between the parameters does not arise. If activity coefficient data must be used and parameters from two different least squares fits must be combined, then activity coefficient values for each component in the mixtures should also be predicted using one of several proposed models (Reilly et al., 1971; Lietzke and Stoughton, 1972; Scatchard et al., 1970). If much disparity is observed between the predicted values and values calculated from the parameters of the least squares fits, then the matrix of correlation coefficients (calculated from the elements of the least squares inverse matrix) should be examined. If large correlations between any of the parameters are observed, then the predicted values are to be preferred as estimates of the activity coefficients of the components of the mixture.

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