Problems Encountered in Deriving Activity Coefficient Values from Data on Mixed Electrolyte Systems

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Difficulties which may be encountered in deriving activity coefficients 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 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 sources 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 osmotic technique (Robinson and Stokes, 1963). A well-known solution of varying total ionic strength and composition is equilibrated isopiestically 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 ratio so obtained the osmotic coefficients of the mixed electrolyte solutions are calculated. The osmotic coefficient values may be fitted by the method of least squares to a high speed computer to an equation expressing the osmotic coefficient as a function of total ionic strength, 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 as appropriate expressions to calculate the activity coefficient of each component (electrolyte) in the mixture.

Wherever experimental data, such as those presented in Tables 1 and 2, are used, the activity coefficients are fitted by least squares to a mathematical expression to obtain...
for the $B_2$-$C_{12}$ correlation was 0.999, while the remaining coefficients lay between 0.65 and $\pm 0.65$. 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 in 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-$\text{Na}_2\text{ZnBr}_4$ system alone, computed from parameters obtained from the simple equation 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 coefficients of both salts in the mixture.

Other three-electrolyte systems that have been investigated by the foregoing technique include HCI:HCl:CaCl$_2$ (Lietzke and Daftburg, 1972), HCl:HCl:CaCl$_2$ (Lietzke et al., 1969), HCl:NaCl:LiCl (Lietzke and Danford, 1972), and HCl:LiCl:CaCl$_2$ (Lietzke and Danford, 1973). In no case was the problem of correlation as severe as in these systems as in the HBr:NaBr-$\text{ZnBr}_2$ system, although moderate disagreement was observed between predicted and fitted values of the activity coefficients of the CaCl$_2$ and the LiCl in their respective mixtures. In all two-electrolyte and three-electrolyte systems that have been investigated by the foregoing techniques, the best agreement between the log $\gamma$ values calculated from the parameters of the fits and predicted log $\gamma$ values was observed with mixtures involving smaller cations.

### Summary

In view of the difficulties associated with treating thermodynamic data on mixed electrolyte systems, the following recommendations are made. When 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 of the derived osmotic coefficient expression are independent of the components. However, if activity coefficient data are not available for both the components, the problem of correlation may be handled by the use of the model of Scatchard (1961) to calculate the 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 Scottburg, 1972; Scatchard et al., 1970). If such correlation does not arise, then the activity coefficient values for the mixture should be predicted using one of several proposed models (Reilly et al., 1971; Lietzke and Scottburg, 1972; Scatchard et al., 1970).

#### Reference


