A Revolutionary Approach to Thermodynamic Property Predictions for Multicomponent Concentrated Aqueous Electrolyte Systems

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Considerable difficulties persist in modeling the thermodynamics of multicomponent aqueous electrolyte solutions, especially at high concentrations. The widely-adopted Pitzer formalism suffers from severe disadvantages particularly with the combinatorial increase in mixing parameters required in multicomponent systems. Alternatively, the simple mixing rules of Young, of Harned and of Zdanovskii have been employed to predict the properties of mixtures using only the properties of the binary constituents with few or no additional parameters. Among these, Zdanovskii's rule is particularly promising because it constitutes a fundamental criterion for ideal mixing, i.e. when solutions having the same solvent activity are mixed in any proportion, the solvent activity remains unchanged. Many mixtures are known from experiment to obey Zdanovskii's rule. However, the application to aqueous electrolyte systems of practical interest has been hindered because the accurate determination of water activity using the Gibbs-Duhem relation is process-intensive. This paper describes an alternative method which efficiently calculates the water activity of a multicomponent solution obeying Zdanovskii's rule. Some specific examples of the method will be presented and various applications considered. In some systems, where deviations from Zdanovskii's rule occur, a single empirical parameter can be obtained and easily incorporated into the method.