

Quantifying Ion-Ion Association in Mixed Electrolyte Systems Using Bulk Thermodynamic Experimental Data

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Activity coefficient models for electrolyte solutions, such as the equations of Pitzer or of eNRTL, have been used in the past to obtain the experimental values of the Kirkwood-Buff integrals (KBIs) for bulk single electrolyte solutions. The KBIs in a single electrolyte solution quantify the salt-solvent, salt-salt, and solvent-solvent net affinities, and are derived from bulk thermodynamic volumetric and chemical potential composition-derivative data. In this simplest case, it is also widely known how to re-interpret these KBIs to obtain the ion-specific KBIs (cation-solvent, cation-anion, *etc.*). However, this process has never been performed for systems with more than one species of cation and anion, which is a severe restriction. Here we show, for the first time, how to carry out the process for bulk mixed electrolyte solutions regardless of ion concentration, valency, molecular complexity, *etc.*, assuming one has correlating equations for the bulk thermodynamic data. This is made possible by combining Kirkwood-Buff theory and local electroneutrality constraints. We will use the Pitzer activity coefficient model to illustrate the process for bulk mixtures for the reciprocal salt systems NaCl+KBr (*aq*) at 298 K and 1 bar and MgCl₂+KBr (*aq*) at 373 K and 1 bar as well as their common ion and single salt subsystems; however, the process could be carried out for any number of ionic components. A comparison of the experimental ion-specific KBIs to those obtained from molecular dynamics simulations of the same systems is provided and are shown to be in excellent agreement for the ambient NaCl+KBr (*aq*) system using the KBFF+SPC/E force field.