Density gradients in aqueous salt solutions: a challenging calculation for electrolyte equations of state

Iván Cubilla, Marcos Cáceres, Christian E. Schaerer, Marcelo Castier

Abstract

In clinical laboratories around the world, isopycnic separations are routinely used to separate biological materials based on density differences. One of the techniques to form a density gradient for such separations is to centrifuge an aqueous salt solution. The high angular speeds, salt concentration and pressure can reach high values, creating challenging conditions for the modeling of centrifugation equilibrium. This paper addresses this problem and presents a formulation and a solution procedure for determining the thermodynamic equilibrium of electrolyte solutions during centrifugation. This is accomplished by a nested-loop algorithm; the outer loop iterates on the liquid volume; the inner loop minimizes the Helmholtz function at the given temperature and component amounts, for the current volume value. The Helmholtz function is evaluated as the summation of an intrinsic contribution given by the eSAFT-VR Mie equation of state, an external contribution of the centrifugal field, and induced electrostatic contribution associated with the possible displacement of charged species in the system. In general, qualitative agreement between the experimental and calculated density profiles was observed in the three systems studied.