

Mixing electrolytes in water at elevated temperatures and pressures: Experimental and molecular dynamics insights

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Aqueous fluids containing electrolytes are the essential components of many geological environments. Such saline solutions form economic mineral deposits, are the primary medium of heat extraction from geothermal reservoirs, determine potential dispersion of nuclear and chemical waste components from repositories, and control the efficiency of CO₂ sequestration in deep aquifers. Our knowledge of properties of mixed electrolyte solutions at conditions typical for the Earth's upper crust however is still deficient; thus researchers currently cannot accurately model geochemical behavior of these fluids and evaluate processes such as dissolution and precipitation of minerals, or gas solubilities.

Recent experimental data [1-3] shed light on volumetric properties of ternary aqueous electrolyte mixtures at the wide range of temperatures, pressures and compositions. These data can also be used to obtain information about structure and interactions among ions and molecules in a solution. In order to expand our understanding of complex aqueous solutions, molecular simulations were performed. We present the results of molecular dynamics (MD) calculations on mixtures of chlorides and sulfates of Na, K, Ca and Mg, complementing our experimental volumetric measurements of the same aqueous electrolyte solutions. Simulations were performed for various concentrations of solutes in water solvent (SPC/E model) at temperatures up to 250 °C and pressures up to 100 MPa.

Variations of volumes of mixing for electrolyte solutions derived from experimental measurements are compared to those from molecular model. The mixing effects examined on the molecular level from MD simulations are related to changes in the structure of solution – alteration of hydration shells, formation of ion pairs and complex clusters. These insights into the microscopic structure and effects of mixing form a rigorous basis for developing mixing rules for thermodynamic models essential for equilibrium calculations in numerous geochemical applications.

[1] Zezin et al. (2014) *J.Chem.Eng.Data*, **59** (3), 736-749.

[2] Zezin et al. (2014) *J.Chem.Eng.Data*, **59** (8), 2570-2588.

[3] Zezin et al. (2015) *J.Chem.Eng.Data*, 10.1021/je501152a