

Osmotic Coefficients, Solubilities, and Deliquescence Relations in Mixed Aqueous Salt Solutions at Elevated Temperature

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While thermodynamic properties of pure aqueous electrolytes are relatively well known at ambient temperature, there are far fewer data for binary systems extending to elevated temperatures and high concentrations. There is no general theoretically sound basis for prediction of the temperature dependence of ionic activities, and consequently temperature extrapolations based on ambient temperature data and empirical equations are uncertain and require empirical verification. Thermodynamic properties of mixed brines in a wide range of concentrations would enhance the understanding and precise modeling of the effects of deliquescence of initially dry solids in humid air in geological environments and in modeling the composition of waters during heating, cooling, evaporation or condensation processes. These conditions are of interest in the analysis of waters on metal surfaces at the proposed radioactive waste repository at Yucca Mountain, Nevada. The results obtained in this project will be useful for modeling the long-term evolution of the chemical environment, and this in turn is useful for the analysis of the corrosion of waste packages.

In particular, there are few reliable experimental data available on the relationship between relative humidity and composition that reveals the eutonic points of the mixtures and the mixture deliquescence RH. The deliquescence RH for multicomponent mixtures is lower than that of pure component or binary solutions, but is not easy to predict quantitatively since the solutions are highly nonideal. In this work we used the ORNL low-temperature and high-temperature isopiestic facilities, capable of precise measurements of vapor pressure between ambient temperature and 250 °C for determination of not only osmotic coefficients, but also solubilities and deliquescence points of aqueous mixed solutions in a range of temperatures. In addition to standard solutions of CaCl₂, LiCl, and NaCl used as references, precise direct-pressure measurements were also made at elevated temperatures. The project included multicomponent mixtures useful for verification of models, and a set of binary solutions with common ions (such as KNO₃ + NaNO₃, KNO₃ + Ca(NO₃)₂, NaNO₃ + Na₂SO₄, and KNO₃ + K₂SO₄) needed for determination of the mixing parameters in the Pitzer ion-interaction model for mixtures. The results are compared with existing experimental results and model predictions.