

Thermodynamic Modeling of Aqueous Systems Containing Amines and Amine Hydrochlorides

Malgorzata Lencka, Jerzy Kosinski, Peiming Wang and Andrzej Anderko^{C, S}

OLI Systems Inc., Cedar Knolls, NJ, U.S.A.

aanderko@olisystems.com

A comprehensive thermodynamic model has been developed for calculating the thermodynamic properties of aqueous mixtures containing amines and amine hydrochlorides. Various amines, including alkylamines, alkanolamines, and heterocyclic nitrogen derivatives are commonly used to neutralize acidic streams in refinery column overhead units. However, the presence of amines in combination with hydrogen chloride may lead to the formation of solid or concentrated aqueous amine hydrochloride phases, which may cause corrosion problems. Thermodynamic modeling offers the possibility of rationalizing and preventing the formation of amine hydrochlorides in multicomponent mixtures containing amines, water, hydrocarbons, hydrogen chloride, and other acid gases. For this purpose, the previously developed Mixed-Solvent Electrolyte (MSE) model has been extended to amine and amine hydrochloride systems, which may show vapor-liquid, solid-liquid and solid-gas equilibria in aqueous environments. The MSE model represents both solution speciation and phase equilibria. Standard-state properties of individual species are calculated from the Helgeson-Kirkham-Flowers equation of state whereas the excess Gibbs energy includes a long-range electrostatic interaction term expressed by a Pitzer-Debye-Hückel equation, a virial coefficient-type term for interactions between ions and a short-range term for interactions involving neutral molecules. The combined model accurately represents experimental phase equilibrium and pH data for systems ranging from dilute aqueous solutions to pure solid or fused liquid amine hydrochloride phases. When applied to multicomponent systems encountered in refinery overheads, the model can be used to simulate the changing phase behavior of condensing streams, which may include stability regions of a gas phase, a concentrated amine hydrochloride ionic phase, a dilute aqueous phase, a volatile solid phase, and a hydrocarbon-rich liquid phase.