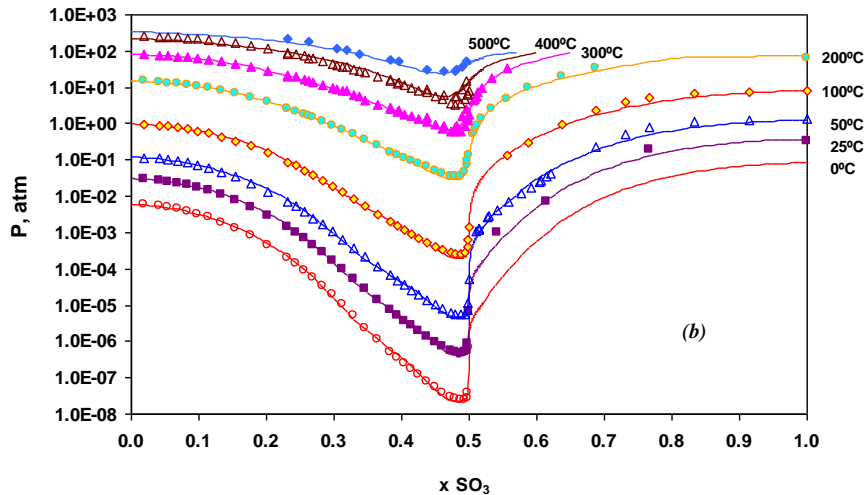OLI systems, Inc.

OLI Mixed Solvent Electrolyte (MSE) Model

Vapor-liquid equilibria for the system $H_2SO_4 - SO_3 - H_2O$

In a multi-component system, the partial molal Gibbs energy of the i-th species is related to the molality (m_i)

by $\overline{G}_i = \overline{G}_i^0 + RT \ln m_i \gamma_i$

where $\overline{G}_i^0$ is the standard-state partial Gibbs energy and γ_i is the activity coefficient. The thermodynamic properties of the system can be calculated if the standard-state Gibbs energies are available for all species as functions of temperature and pressure (i.e., $\overline{G}_i^0(T,P)$) and the activity coefficients are known as functions of the composition and temperature (i.e., $\gamma_i(\mathbf{m},T)$).

STANDARD STATE : EQUATION OF STATE

The key to representing the standard-state properties over substantial temperature and pressure ranges is the accurate knowledge of the heat capacity and volume. For this purpose, the Helgeson-Kirkham-Flowers-Tanger (HKFT) equation of state is used. This equation accurately represents the standard-state thermodynamic functions for aqueous, ionic or neutral, species as functions of both temperature and pressure. In its revised form, the HKT equation of state is capable of reproducing the standard-state properties up to 1000 °C and 5 kbar.

The HKFT equation is based on the solvation theory and expresses the standard-state thermodynamic functions as sums of structural and solvation contributions, the latter being dependent on the properties of the solvent (i.e., water). The HKFT equation expresses the heat capacity and volume as functions of pure water properties and seven empirical parameters, which have been tabulated for large numbers of ions, complexes and neutral, both inorganic and organic, molecules. The remaining thermodynamic properties are obtained by thermodynamic integration using the values of the Gibbs energy, enthalpy and entropy at reference temperature and pressure as integration constants. Further, estimation techniques are available for species for which no experimental data are available.

ACTIVITY COEFFICIENT MODEL

The activity coefficient model has been designed by OLI to cover a wide range of chemistries including electrolyte, non-electrolyte and mixed systems. The excess Gibbs energy is expressed as

$$\frac{G^{ex}}{RT} = \frac{G_{LR}^{ex}}{RT} + \frac{G_{MR}^{ex}}{RT} + \frac{G_{SR}^{ex}}{RT}$$

where G_{LR}^{ex} represents the contribution of long-range electrostatic interactions, G_{SR}^{ex} is the short-

range contribution resulting from intermolecular interactions, and an additional (middle-range) term G_{MR}^{ex} represents primarily ionic interactions (i.e., ion/ion and ion/molecule) that are not accounted for by the long-range term. The long-range interaction contribution is calculated from the Pitzer-Debye-Hückel

formula. For the short-range interaction contribution (primarily between neutral molecules), the UNIQUAC equation is used. The ionic interaction contribution, which is the key to representing electrolyte properties, is calculated from an ionic strength-dependent, symmetrical second virial coefficient-type expression:

$$\frac{G_{MR}^{ex}}{RT} = -\left(\sum_i n_i\right)\sum_i\sum_j x_i x_j B_{ij}(I_x)$$

where $B_{ij}(I_x) = B_{ji}(I_x)$, $B_{ii} = B_{jj} = 0$ and the ionic strength dependence of B_{ij} is given by

$$B_{ij}(I_x) = b_{ij} + c_{ij}\exp(-\sqrt{I_x + a_1})$$

where b_{ij} and c_{ij} are adjustable, temperature-dependent parameters. To calculate the fugacities of components in the gas phase, the Redlich-Kwong-Soave equation of state is used.

SPECIATION

Speciation effects due to the formation of ion pairs and complexes are explicitly taken into account using chemical equilibria. For this purpose, the standard-state chemical potentials for aqueous species are calculated as functions of temperature and pressure using the HKFT equation of state. For speciation calculations in organic or mixed-solvent electrolyte solutions, the chemical potential of the species is modeled by combining aqueous standard-state properties with Gibbs energies of transfer between aqueous and nonaqueous environments.

TRANSPORT PROPERTIES

Separate models have been developed for calculating viscosity, electrical conductivity and self-diffusivity of aqueous and mixed-solvent electrolyte solutions.
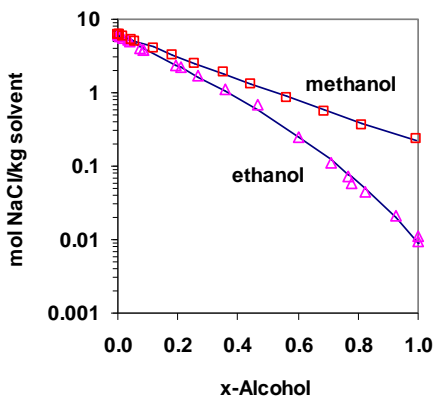
Solubility of NaCl in methanol-H_2O and ethanol-H_2O mixtures

VALIDITY RANGE

Chemistries including, but not limited to:

- Aqueous electrolytes ranging from infinite dilution to fused salts or pure acids or other solutes
- Electrolyte systems in organic and mixed solvents
- Nonelectrolyte systems

Temperatures up to 0.9 of the critical temperature of the mixture. For aqueous systems, this usually translates to ~300 °C, but higher temperatures can be reached as long as the system is subcritical.