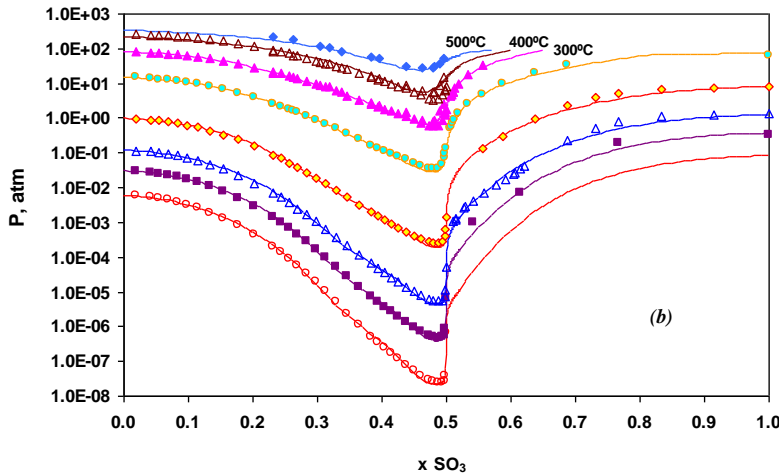


# Mixed Solvent Electrolyte (MSE) Thermodynamic Model

The Mixed-Solvent Electrolyte (MSE) model is an advanced excess free energy theory that expands the prediction range for solutions containing electrolytes and non-electrolytes. MSE is the product of theoretical advances made from strong-electrolyte theories. The result of this advancement is elimination of the ionic strength limits and the requirements that the continuous solvent phase is water. Now, calculations are possible when the process is a wet salt or when the solvent is an acid, alcohol or other material.

MSE is now the model of choice where extreme compositions or conditions are encountered, and is critical when modelling the following systems:



- ✓ Salt solubility that reaches the fused salts limit (e.g., nitrates)
- ✓ Miscible solvents or pure acids mixtures (e.g., oleum)
- ✓ Electrolytes dissolved in non-aqueous solvents (ionic liquids, glycols, etc.)
- ✓ Extreme pressure chemistry (CO<sub>2</sub> sequestration)
- ✓ Conditions approaching critical temperature (accurate to 90% of T<sub>c</sub>)
- ✓ Electrolyte solubility in liquid hydrocarbon phases.
- ✓ Salt desublimation from the vapor phase.

A system's thermodynamic properties are calculated from two sources; the first is from the T & P-dependent standard-state Gibbs energies (i.e.,  $\bar{G}_i^0(T, P)$ ) of each species present. The second is from the T, P and composition dependent excess Gibbs energy (i.e.,  $\gamma_i(\mathbf{m}, T)$ ) for each species present. In the combined relationship, the partial molal Gibbs energy of the *i*<sup>th</sup> species is,  $\bar{G}_i = \bar{G}_i^0 + RT \ln m_i \gamma_i$ , where  $\bar{G}_i^0$  is the standard-state partial Gibbs energy and  $\gamma_i$  is the activity coefficient. This activity coefficient,  $\gamma_i$ , is computed using the new MSE theory.

## Mixed Solvent Electrolyte constructs

The MSE model computes the excess Gibbs energy (the energy change that impacts a species activity coefficient). It is a function of three energy terms: 1) long-range electrostatic interactions, 2) specific ion-ion and ion-molecule interactions, and 3) short range interactions. A complete explanation of each contributing parameter is provided in Wang et al. (2002)<sup>1</sup>.

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

The long-range interactions are quantified using the Pitzer-Debye-Hückel formula.

$$\frac{G_{DH}^{ex}}{RT} = - \left( \sum_i n_i \right) \frac{4A_x I_x}{\rho} \ln \left( \frac{1 + \rho I_x^{1/2}}{\sum_i x_i [1 + \rho (I_{x,i}^0)^{1/2}]} \right)$$

<sup>1</sup> Wang, P., A. Anderko, and R.D. Young. 2002. A speciation-based model for mixed-solvent electrolyte systems. Fluid Phase Equilibria, vol. 203, pp.141-176

## Mixed Solvent Electrolyte (MSE) Thermodynamic Model

The specific ion-ion and ion-molecule interactions are calculated from an ionic strength-dependent, symmetrical second virial coefficient-type expression; this is key to modeling concentrated electrolytes:

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

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

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

The short-range dispersive and polar interactions (primarily between neutral molecules) are computed using the UNIQUAC equation is used (details can be found elsewhere).

$$\frac{G_{UNIQUAC}^{ex}}{RT} = \frac{G_{combinatorial}^{ex}}{RT} + \frac{G_{residual}^{ex}}{RT}$$

### Speciation

Speciation, including ion pair and complex formation, is quantified using chemical equilibrium equations. The intrinsic equilibrium constants are calculated using the Helgeson-Kirkham-Flowers-Tanger equation of state. This equation accurately quantifies the standard-state thermodynamic properties as functions of temperature and pressure. In its implemented form, this equation of state reproduces standard-state properties up to 1000 °C and 5 kbar.

To predict speciation in organic or mixed-solvent electrolyte solutions, the aqueous standard-state properties are combined with Gibbs energies of transfer between aqueous and nonaqueous environments.

### Transport and interfacial properties

MSE contains sub-models to calculate viscosity, electrical conductivity, self-diffusivity, thermal conductivity, and surface and interfacial tension

### Validation materials

OLI has extensive Excel-based validation plots for solutions that MSE model parameters have been established. These plots are available to clients upon request.

