

Summary of Accomplishments: MSE phases I, II, & III

OLI's Mixed Solvent Electrolyte (MSE) model, developed with partial support of the MSE Consortium Phase I, II and III, has provided OLI's customers with a significant advancement for chemical process simulation and other applications. The model offers a tool for solving many problems that, until recently, could not be addressed using any commercial simulators. The continued development of the MSE model and databank promises many new benefits for industrial users of the technology.

OLI is continuing the MSE Consortium, via a Phase IV, to help achieve support and steer the further development of the Mixed Solvent Electrolyte framework and databank. In the early stage, OLI benefited greatly from funding from the US DOE, in two separate projects, which has provided about \$1.0M to support this work. In addition, OLI, as noted above, also benefited from industry support through the MSE Consortium Phase I, II and III.

At present, OLI Systems is in the final months of Phase III of the MSE model development and parameterization project. During the course of this project, we have achieved the following objectives:

- 1. *A comprehensive thermodynamic model for the calculation of phase equilibria, speciation, caloric properties and density.*** With this model, we have obtained unparalleled accuracy in reproducing experimental data for systems containing electrolytes in water, organic or mixed solvents ranging from infinite dilution to the pure solute or fused salt limit. The details of this model can be found in the following papers, which are available in the OLI Resource Library:

 - P. Wang, A. Anderko and R.D. Young, "A Speciation-Based Model for Mixed-Solvent Electrolyte Systems", *Fluid Phase Equilibria*, 203 (2002) 141-176.
 - A. Anderko, P. Wang and M. Rafal, "Electrolyte Solutions: From Thermodynamic and Transport Property Models to the Simulation of Industrial Processes", *Fluid Phase Equilibria*, 194-197 (2002) 123-142.
 - P. Wang, R.D. Springer, A. Anderko and R.D. Young, "Modeling Phase Equilibria and Speciation in Mixed-Solvent Electrolyte Systems", *Fluid Phase Equilibria*, 222-223 (2004) 11-17.
 - P. Wang, A. Anderko, R. D. Springer, and R. D. Young, "Modeling Phase Equilibria and Speciation in Mixed Solvent Electrolyte Systems. II. Liquid-liquid equilibria and properties of associating electrolyte solutions", *J. Molec. Liquids*, 125 (2006) 37-44.
 - J.J. Kosinski, P. Wang, R.D. Springer and A. Anderko, "Modeling Acid-Base Equilibria and Phase Behavior in Mixed-Solvent Electrolyte Systems" *Fluid Phase Equilibria*, 256 (2007) 34-41.
 - M.S. Gruskiewicz, D.A. Palmer, R.D. Springer, P. Wang and A. Anderko, "Phase Behavior of Aqueous Na – K – Mg – Ca – Cl – NO₃ Mixtures: Isopiestic Measurements and Thermodynamic Modeling" *J. Solution Chem.*, 36 (2007) 723-765.
- 2. *A databank of model parameters for more than 1500 species for general-purpose calculations (MSEPUB), supplemented by two specialized databanks for corrosion-related (CRMSE) and geochemical (GEMSE) calculations.*** These databanks cover the chemistry of widely encountered electrolyte and nonelectrolyte systems as well as specific systems of compelling interest to our industrial sponsors. The actual chemical systems covered by

parameters projected through the end of the current MSE III project are shown in Appendix 1 of this document.

3. ***The ability to compute very complex phase combinations including LLE with two electrolyte phases.*** The OLI Engine has been extensively upgraded to work in the full range of concentrations. It can accurately compute solid-liquid equilibria in systems with multiple competing solid phases, liquid-liquid equilibria with electrolyte speciation in both coexisting phases, solid-gas equilibria and it can deal with substantially extended temperature ranges – well below 0°C and above 300°C, provided that the temperature is roughly below 0.9 of the critical temperature of the mixture.
4. ***Models and databank development for principal transport properties including viscosity, electrical conductivity, thermal conductivity, and self-diffusivity.*** With these models, the users have the capability to simulate these transport properties for aqueous, nonaqueous or mixed-solvent systems in the same range of concentration and temperature that is covered by the thermodynamic model. The details of these models are available in the following papers:
 - P. Wang and A. Anderko, “Modeling Self-Diffusion in Mixed-Solvent Electrolyte Solutions”, *Ind. Eng. Chem. Res.*, 42 (2003) 3495-3504.
 - P. Wang, A. Anderko and R.D. Young, “Modeling Viscosity of Concentrated and Mixed-Solvent Electrolyte Systems”, *Fluid Phase Equilibria*, 226 (2004) 71-82.
 - P. Wang, A. Anderko and R.D. Young, “Modeling Electrical Conductivity of Concentrated and Mixed-Solvent Electrolyte Systems”, *Ind. Eng. Chem. Res.*, 43 (2004) 8083-8092.
 - P. Wang and A. Anderko, “Modeling Thermal Conductivity of Concentrated and Mixed-Solvent Electrolyte Systems”, *Ind. Eng. Chem. Res.*, 47 (2008) 5698-5709.

The work on developing a surface tension model is currently in progress.

5. ***A software implementation of MSE under both ESP (starting with version 7.0, currently 8.0) and the Analyzers (version 2.0 with version 3.0 being available as a beta).*** In addition, the MSE model and databanks are available in the OLI Engine for Aspen Plus, UNISIM, OLI Pro, and PRO/II.
6. ***Implementation of stability diagrams in conjunction with MSE.*** Stability diagrams (i.e., the real solution Pourbaix diagrams, the species-species and yield diagrams) can be generated using the mixed-solvent model. Thus, thermodynamics of corrosion can be studied using the MSE as well as the aqueous model.
7. ***Implementation of a more predictive correlations for calculating the heat and mass transfer coefficients to enable predictive calculations for heat- and mass-transfer limited packed towers.*** These facilities have been implemented in ESP, UNISIM and OLI Pro. Gas-phase transport properties have also been implemented to support these calculations. Upon completion of the surface tension model, it will be integrated with these correlations and the last missing piece of information will be provided to calculate mass transfer coefficients.
8. ***Modeling surface phenomena in conjunction with MSE.*** Computation of ion exchange, molecular adsorption and surface complexation has been enabled in conjunction with the MSE model. Further, a new solid-phase activity coefficient model based on the Wilson equation has been implemented to improve accuracy for multicomponent solutions.

Appendix 1: Chemistry Covered in MSE III

1. Binary and principal ternary systems composed of the following primary ions and their hydrolyzed forms:

Cations: Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , NH_4^+

Anions: Cl^- , F^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , OH^-

2. Multicomponent Na salts

Na^+ - F^- - NO_3^- - NO_2^- - CO_3^{2-} - SO_4^{2-} - OH^-

3. Li chemistry

Li^+ - K^+ - Mg^{2+} - Ca^{2+} - Cl^-

4. Ba chemistry

Ba^{2+} - Cl^- - CO_3^{2-} - SO_4^{2-} - OH^- - BO_2^- - Na^+ - K^+ - Mg^{2+} - Ca^{2+}

5. Borate chemistry

H^+ - Li^+ - Na^+ - Mg^{2+} - Ca^{2+} - BO_2^- - OH^-

H^+ - Li^+ - Na^+ - BO_2^- - HCOO^- - CH_3COO^- - Cl^- - OH^-

6. Aqueous acids, associated acid oxides and acid-dominated mixtures

H_2SO_4 - SO_3

HNO_3 - N_2O_5

HNO_2

H_3PO_4 - $\text{H}_4\text{P}_2\text{O}_7$ - $\text{H}_5\text{P}_3\text{O}_{10}$ - P_2O_5

H_3PO_2

H_3PO_3

HF

HCl

HBr

HI

H_3BO_3

$\text{CH}_3\text{SO}_3\text{H}$

$\text{NH}_2\text{SO}_3\text{H}$

HFSO_3 - HF - H_2SO_4

HI - I_2 - H_2SO_4

HNO_3 - H_2SO_4 - SO_3

H_3PO_4 with various calcium phosphates

H^+ - Na^+ - Cl^- - NO_3^-

H^+ - Na^+ - Cl^- - F^-

H^+ - Na^+ - PO_4^- - OH^-

H^+ - NH_3 - NO_3^- - SO_4^{2-}

H^+ - NH_3 - Cl^-

7. Sulfide and H_2S chemistry (other than transition metals)

NH_4HS - H_2S - NH_3

H_2S - H^+ - Na^+ - Cl^-

Na_2S - NaHS - H_2S

8. Inorganic gases in aqueous systems

CO₂ - NH₃ - H₂S
SO₂ - H₂SO₄
N₂
O₂
H₂ - H⁺ - Na⁺ - Cl⁻

9. Silica chemistry

Si^{IV} - H⁺ - OH⁻ - Na⁺

10. Hydrogen peroxide chemistry

H₂O₂ - H₂O - H - Na - OH - SO₄ - NO₃

11. Transition metal aqueous systems

Fe^{II} - H⁺ - OH⁻ - Cl⁻ - Br⁻ - SO₄²⁻ - NO₃⁻ - S²⁻ - Ac⁻ - NH₃ - NH₄⁺ - Na⁺
Fe^{II} - Cr^{III} - H⁺ - OH⁻
Fe^{III} - H⁺ - Cl⁻ - SO₄²⁻ - NO₃⁻
Ni^{II} - H⁺ - OH⁻ - Cl⁻ - SO₄²⁻ - NO₃⁻ - PO₄³⁻ - S²⁻ - NH₃ - Na⁺ - morpholine
Ni^{II} - Cr^{III} - H⁺ - OH⁻
Ni^{II} - Ti^{IV} - H⁺ - OH⁻
Ni^{II} - Fe^{II} - H⁺ - OH⁻ - BO₂⁻
Cr^{III} - H⁺ - OH⁻ - Cl⁻ - SO₄²⁻ - NO₃⁻
Cr^{VI} - H⁺ - OH⁻ - NO₃⁻
Mo^{III} - H⁺ - Cl⁻ - OH⁻ - H₂
Mo^{IV} - H⁺ - Cl⁻ - OH⁻ - H₂
Mo^{VI} - H⁺ - OH⁻ - Cl⁻ - SO₄²⁻ - NO₃⁻
W^{VI} - H⁺ - OH⁻ - Na⁺ - Cl⁻, NO₃⁻
W^{IV} - H⁺ - OH⁻
Sn^{II} - H⁺ - OH⁻ - CH₃SO₃⁻
Sn^{IV} - H⁺ - OH⁻ - Cl⁻
Zn^{II} - H⁺ - Cl⁻ - SO₄²⁻ - NO₃⁻
Zn^{II} - Li⁺ - Cl⁻
Cu^{II} - H⁺ - OH⁻ - Cl⁻ - SO₄²⁻ - NO₃⁻ - H₂S - S²⁻ - CO₂ - CO₃⁻ - NH₃ - Na⁺ - morpholine - Et₂NH
Cu^I - H₂S - S²⁻
Cu^{II} - Cu^I - Fe^{II} - Fe^{III} - H⁺ - OH⁻ - S²⁻
Ti^{IV} - H⁺ - OH⁻ - Ba²⁺ - Cl⁻ - OH⁻ - BuO⁻ - Na⁺
Pb^{II} - H⁺ - OH⁻ - Na⁺ - Cl⁻ - SO₄²⁻ - S²⁻ - H₂S - CO₃²⁻ - ClO₄⁻ - K⁺ - Si⁴⁺
Pb^{II} - Ti^{IV} - H⁺ - OH⁻
Pb^{IV} - H⁺ - OH⁻

12. Miscellaneous inorganic systems in water

NH₂OH
Na₂S₂O₃
Na⁺ - BH₄⁻ - OH⁻
Na⁺ - SO₃²⁻ - SO₂ - OH⁻
HCN - NaCN

13. Most elements from the periodic table in their elemental form

14. Base ions and hydrolyzed forms for the majority of elements from the periodic table

15. Organic acids/salts in water and alcohols

Formic

H^+ - Li^+ - Na^+ - Formate - OH^-

Formic acid – MeOH - EtOH

Acetic

H^+ - Li^+ - Na^+ - K^+ - Ca^{2+} - Ba^{2+} - Acetate - OH^-

Acetic acid – MeOH – EtOH – CO_2

Citric

H^+ - Na^+ - Citrate - OH^-

Oxalic

H^+ - Oxalate – Cl^- - SO_4^{2-} , NO_3^- , MeOH, EtOH, 1-PrOH

Malic

Glycolic

Adipic

H^+ - Na^+ - Adipate

Adipic acid – MeOH, EtOH

Nicotinic

H^+ - Na^+ - Nicotinate

Nicotinic acid - EtOH

Terephthalic

H^+ - Na^+ - Terephthalate

Terephthalic acid – MeOH, EtOH

Isophthalic

Isophthalic acid - EtOH

Trimellitic

Trimellitic acid - EtOH

16. Hydrocarbon systems

Hydrocarbon + H_2O systems

Straight chain alkanes: C1 through C30

Isomeric alkanes: isobutane, isopentane, neopentane

Alkenes: ethene, propene, 1-butene, 2-butene, 2-methylpropene

Aromatics: benzene, toluene, o-, m-, p-xylenes, ethylbenzene, cumene, naphthalene, anthracene, phenantrene

Cyclohexane

Hydrocarbon + salt generalized parameters

H^+ , NH_4^+ , Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , OH^- , HCO_3^- , CO_3^{2-} , NO_3^- , SO_4^{2-}

17. Organic solvents and their mixtures with water

Alcohols

Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, cyclohexanol

Glycols

Mono, di- and triethylene, propylene, polyethylene glycols

Phenols

Phenol, catechol

Ketones

Acetone, methylisobutyl ketone

Aldehydes

Butylaldehyde

Carbonates

Diethylcarbonate, propylene carbonate

Halogen derivatives

Chloroform, carbon tetrachloride

Amines (including mixtures with hydrocarbons)

Alkylamines:

Primary: methylamine, ethylamine, n-butylamine, cyclohexylamine, thylenediamine, 3-methoxypropylamine

Secondary: dimethylamine, diethylamine

Tertiary: trimethylamine, triethylamine, tri-n-octylamine

Mixed amines: methylamine – dimethylamine – trimethylamine

Alkanolamines

methyldiethanolamine

Heterocyclic amines

N-methylpyrrolidone, morpholine, 2,6-dimethylmorpholine

Aminoacids

Methionine

Nitriles

Acetonitrile

Amides

Dimethylacetamide, dimethylformamide

18. Polyelectrolytes

Polyacrylic acid

Complexes with Cu, Zn, Ca, Fe(II), Fe(III)

19. Mixed-solvent inorganic/organic system

Methanol – salt systems

Methanol – H^+ – Na^+ – K^+ – Mg^{2+} – Ca^{2+} – Cl^- – CO_3^{2-} – HCO_3^- – SO_4^{2-} – BO_2^- – $HCOO^-$ – CH_3COO^- – CO_2 – H_2S

Glycol – salt systems

Mono, di- and triethylene glycols – H^+ – Na^+ – K^+ – Mg^{2+} – Ca^{2+} – Ba^{2+} – Cl^- – CO_3^{2-} – HCO_3^- – SO_4^{2-} – BO_2^- – CH_3COO^- – CO_2 – H_2S

Ethanol – salt systems

Ethanol – Li^+ – Na^+ – Cl^-

Ethanol – O_2

Phenol - acetone - SO_2 - HFo - HCl – H_2O

n-Butylaldehyde – $NaCl$ - H_2O

$LiPF_6$ – diethylcarbonate – propylene carbonate

Phenol - acetone - SO_2 - HFo - HCl – H_2O

n-Butylaldehyde – $NaCl$ - H_2O

$LiPF_6$ – diethylcarbonate – propylene carbonate

20. Mixed-solvent organic systems

HAc – tri-n-octylamine – toluene – H_2O

HAc – tri-n-octylamine – methylisobutylketone – H_2O

Dimethylformamide – HFo – H_2O

MEG – EtOH – H_2O

Further developments projected by the end of MSE III (3/31/2009)

Thermophysical framework

Development of a new surface tension model

Development of model parameters

Focus group: Refinery overhead consortium (in collaboration with SwRI)

Modeling hydrometallurgical systems (University of Toronto)

Extension of organic acid chemistry

HI – I₂ – H₂SO₄ – SO₂ – HF system

Preliminary investigation of ionic liquids

Improvement of systems containing light components at high pressures

Phase II of oil and gas-related chemistry

Ethylene oxide systems