It’s Not Magic…
Just Great Technology

Advances in Technology: Properties of Mixed-Solvent Electrolyte Systems

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OLI 35th Anniversary User Conference
October 5-6, 2005
A Comprehensive Model for Aqueous and Mixed-Solvent Electrolyte Systems

Objectives:

- Reproduce speciation and chemical equilibria as well as phase equilibria
- Accurately reproduce
  - Aqueous electrolytes ranging from dilute solutions to fused salts or pure solutes
  - Electrolytes in organic solvents
  - Water-organic-salt systems in the full range of concentrations
  - Cover temperatures up to 0.9 \( T_c \) of the mixture
- Consistently treat phase and chemical equilibria, enthalpy, heat capacity and density
- Predict transport properties using associated models that cover the same range of applicability as the thermodynamic model
Outline of the Thermodynamic Model

Excess Gibbs energy:

\[ \frac{G^{ex}}{RT} = \frac{G_{LR}^{ex}}{RT} + \frac{G_{LC}^{ex}}{RT} + \frac{G_{II}^{ex}}{RT} \]

**LR**  Debye-Hückel theory

**LC**  Local composition model (UNIQUAC) for neutral molecule interactions

**II**  Ionic interaction term for ion-ion and ion-molecule interactions

\[ \frac{G_{II}^{ex}}{RT} = -\left( \sum_i n_i \right) \sum_i \sum_j x_i x_j B_{ij} (I_x) \]
Combining the $G^E$ Model with Chemical Equilibria

- **Standard-state properties**
  - Thermochemical databases for aqueous systems
  - Helgeson-Kirkham-Flowers-Tanger model for T and P dependence
  - Gibbs energy of transfer between water and nonaqueous solvents

- **Activity coefficients**
  - Defined using symmetrical normalization
  - Converted to unsymmetrical normalization to work with standard-state properties in aqueous systems

Predictions over wide concentration and temperature ranges:

VLE for $\text{H}_2\text{SO}_4 + \text{SO}_3 + \text{H}_2\text{O}$:

Pure $\text{H}_2\text{SO}_4$ ($x_{\text{SO}_3} = 0.5$)
Prediction of speciation for \( \text{H}_2\text{SO}_4 + \text{SO}_3 + \text{H}_2\text{O} \)

- Phase equilibria and speciation can be reproduced simultaneously if protons are treated as solvated entities, i.e., as \( \text{H}_3\text{O}^+ \) ions.

Pure \( \text{H}_2\text{SO}_4 (x_{\text{SO}_3} = 0.5) \)
Nitric acid: Vapor-liquid equilibria

![Graph showing vapor-liquid equilibria for nitric acid at different temperatures (25C to 120C).](image-url)
Mixed acids: $\text{H}_2\text{SO}_4 + \text{HNO}_3$

- Parity plot to verify the representation of partial and total pressures

![Parity plot representing the comparison between experimental and predicted pressures for mixed acids $\text{H}_2\text{SO}_4 + \text{HNO}_3$. The plot includes data points for different components: $P$, $\text{PH}_2\text{O}$, $\text{PHNO}_3$, and $\text{PSO}_3$. The plot shows a close alignment with the linear regression line, indicating a good representation of the pressures.](image-url)
Solubility of solids:
Aluminum solubility in alkaline solutions (Bayer process)

$\text{Al}_2\text{O}_3$ wt% vs. $\text{Na}_2\text{O}$ wt%

Graph showing solubility curves for different temperatures:
- $200 \degree C$
- $110 \degree C$
- $95 \degree C$
- $50 \degree C$
- $30 \degree C$
- $25 \degree C$

Equations:
- $\text{Al(OH)}_3(s)$
- $\text{AlOOH}(s)$
- $\text{Na}_2\text{O}_2\text{Al}_2\text{O}_3\cdot 2\text{H}_2\text{O}$

Chemical reaction:
$\text{Al(OH)}_3 + \text{NaOH} + \text{H}_2\text{O}$
Liquid-liquid equilibrium systems

- Simultaneous representation of LLE, SLE and VLE including ionization effects, if applicable

Phenol – water

Methyl isobutyl ketone - water
Solubility of benzene in aqueous (NH₄)₂SO₄ and NaCl solutions at 25°C
Solid-liquid equilibria in the ethylene glycol - NaHCO₃ - H₂O system

- Complex solubility behavior with different solid phases precipitating depending on the glycol content and temperature
Acid-base equilibria in mixed solvents: pH in H₂O₂ - H₂O systems

• Self-dissociation of H₂O₂ is analogous to that of water:
  - \( 2\text{H}_2\text{O}_2 = \text{H}_3\text{O}^+ + \text{HO}_2^- \)

• Apparent pH can be obtained using a glass electrode and calculated from the MSE model
Transport properties in the OLI software

• Available transport properties:
  • Diffusivity
  • Viscosity
  • Electrical conductivity

• OLI was the first to develop transport property models for concentrated, multicomponent aqueous solutions

• Recently, the models have been extended to mixed-solvent systems
Transport properties:

Electrical conductivity of $\text{H}_2\text{O} - \text{H}_2\text{SO}_4 - \text{SO}_3$

![Graph showing electrical conductivity of $\text{H}_2\text{O} - \text{H}_2\text{SO}_4 - \text{SO}_3$]
Transport properties:
Viscosity of H$_2$O - H$_2$SO$_4$ - SO$_3$
Conversion of MSE databank to solvated proton basis

- At this moment, two databanks are available
  - **MIXSOL**: $\text{H}^+\text{-based}$
    - To be eliminated as soon as transport property parameters are adjusted in MSEPUB
  - **MSEPUB**: $\text{H}_3\text{O}^+\text{-based}$ (protons are assumed to be solvated in aqueous and nonaqueous environments)
    - Recommended for all calculations that do not require transport properties
    - Already covers a substantially wider spectrum of chemistry than MIXSOL
Current Content of the MSE Databank (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\(^-\)

• Aqueous acids, associated acid oxides and acid-dominated mixtures
  • H\(_2\)SO\(_4\) – SO\(_3\)
  • HNO\(_3\) – N\(_2\)O\(_5\)
  • H\(_3\)PO\(_4\) – H\(_4\)P\(_2\)O\(_7\) – H\(_5\)P\(_3\)O\(_{10}\) – P\(_2\)O\(_5\)
  • H\(_3\)PO\(_2\)
  • H\(_3\)PO\(_3\)
  • HF
  • HCl
  • HBr
  • HI
  • CH\(_3\)SO\(_3\)H
  • NH\(_2\)SO\(_3\)H
  • HFSO\(_3\) – HF – H\(_2\)SO\(_4\)
  • HI – I\(_2\) – H\(_2\)SO\(_4\)
  • HNO\(_3\) – H\(_2\)SO\(_4\) – SO\(_3\)
  • H\(_3\)PO\(_4\) with various calcium phosphates
Current Content of the MSE Databank (2)

- Inorganic gases in aqueous systems
  - NH₃
  - CO₂
  - H₂S
  - SO₂ + H₂SO₄
  - N₂
  - O₂
  - H₂

- Transition metal aqueous systems
  - Fe(II) and Fe(III) oxides, hydroxides, and bromides
  - FeSO₄⁻ H₂SO₄
  - Sn(II) and Sn(IV) oxides and hydroxides
  - Sn(II) methanesulfonate – methanesulfonic acid
  - ZnCl₂ - LiCl
Current Content of the MSE Databank (3)

- Transition metal aqueous systems - continued
  - CuSO$_4$ – H$_2$SO$_4$
  - Cu(NO$_3$)$_2$ – HNO$_3$
  - Fe$_2$(SO$_4$)$_3$ – H$_2$SO$_4$
  - Fe(NO$_3$)$_3$ – HNO$_3$
  - ZnSO$_4$ – H$_2$SO$_4$
  - Zn(NO$_3$)$_2$ – HNO$_3$

- Most elements from the periodic table in their elemental form
- Base ions and hydrolyzed forms for the majority of elements from the periodic table
- Hydrogen peroxide chemistry
  - H$_2$O$_2$ – H$_2$O including acid-base properties
  - H$_2$O$_2$ – NaOH
  - H$_2$O$_2$ – H$_2$SO$_4$
  - H$_2$O$_2$ - NaNO$_3$
Current Content of the MSE Databank

• Miscellaneous inorganic systems in water
  • NH$_2$OH
  • NH$_4$HS + H$_2$S + NH$_3$
  • LiCl – KCl
  • LiCl – CaCl$_2$
  • Na$_2$S$_2$O$_3$

• Organic solvents and their mixtures with water
  • Alcohols: Methanol, ethanol, 1-propanol, 2-propanol, cyclohexanol
  • Glycols: Monoethylene and propylene glycols, polyethylene glycols
  • Phenols: Phenol, catechol
  • Ketones: Acetone, methylisobutyl ketone
  • Aldehydes: Butyaldehyde
  • Carbonates: Diethylcarbonate, propylene carbonate
  • Hydrocarbons: Benzene, toluene, cyclohexane
  • Amines: tri-N-octylamine
  • Nitriles: Acetonitrile
  • Amides: Dimethylacetamide
  • Halogen derivatives: Chloroform
Current Content of the MSE Databank

(5)

• Organic acids in water, methanol and ethanol and their Na salts
  • Formic
  • Acetic (also K salt)
  • Citric
  • Adipic
  • Nicotinic
  • Terephthalic
  • Isophthalic
  • Trimellitic

• Mixed-solvent organic systems
  • Acetic acid – tri-N-octylamine – toluene – water
  • Acetic acid – tri-N-octylamine – methylisobutylketone – water
  • Acetic acid – ethanol – methanol – water
Current Content of the MSE Databank (6)

• **Mixed-solvent inorganic/organic system**
  - Phenol - H₂O - acetone - SO₂ - formic acid - HCl
  - Benzene - H₂O - NaCl and (NH₄)₂SO₄
  - Cyclohexane - H₂O - NaCl
  - n-Butylaldehyde – NaCl - H₂O
  - LiPF₆ – diethylcarbonate – propylene carbonate
  - Ethanol – LiCl - H₂O
  - Monoethylene glycol – H₂O + Na₂CO₃/NaHCO₃, CO₂, NaCl, HCl
  - Methanol - H₂O + NaCl, HCl

• **Polyelectrolytes**
  - Polyacrylic acid – acid-base properties
Typical applications that require the mixed-solvent electrolyte model

- Processes involving concentrated acids (H$_2$SO$_4$, HNO$_3$, HF, etc.)
- Concentrated nitrate systems (fertilizer industry, nuclear waste storage and processing)
- Salt effects on distillation (salting-in, salting-out)
- Crystallization from organic and mixed solvents
- Hydrometallurgical processes, e.g., high-pressure leaching
- Alkanolamine and amine processes
- Phase equilibria in refinery column overheads (precipitation and dissolution of NH$_4$Cl, NH$_4$HS, amine chlorides)
- Systems with concentrated brines as working fluids (completion fluids, refrigeration cycles, etc.)
- Urea plants
- Battery electrolytes
- Systems involving glycols and alcohols with natural brines in oil and gas production and transmission environments
A comprehensive speciation-based thermodynamic model has been developed.

The model reproduces multiple properties (VLE, SLE, LLE, SGE, caloric properties, densities) in multicomponent systems.

The model has been validated for various classes of mixtures:

- Aqueous electrolytes ranging from dilute solutions to molten salts or pure solutes
- Salt–water–organic systems in full concentration ranges
- Associated models for diffusivity, viscosity and electrical conductivity have been developed
Aqueous or Mixed-Solvent Electrolyte Model?

• Aqueous model
  • Advantages:
    ■ Larger existing databank
    ■ The only model available for rates of corrosion
  • Disadvantages:
    ■ Limitations with respect to composition (30 m with respect to electrolytes, \( x=0.3 \) with respect to nonelectrolytes)
    ■ LLE predictions exclude critical solution points (limited to strongly dissimilar phases)

• MSE model
  • Model advantages:
    ■ No limitations with respect to composition
    ■ Reliable predictions for multicomponent concentrated solutions
    ■ Full range of LLE calculations including electrolytes in both phases
  • Methodological advantages
    ■ Multiproperty regressions
    ■ Consistent use of thermochemical properties (no shortcuts like Kfits)
    ■ Rigorous quality assurance
  • Disadvantages:
    ■ Much smaller existing databank but it is continuously extended