Electrolytes

Process Modeling Using Aspen Plus

Lesson Objectives

- Introduce the electrolyte capabilities in Aspen Plus

Aspen Plus References:

User Guide, Chapter 6, **Specifying Components**

Physical Property Methods and Models Reference Manual, Chapter 5, **Electrolyte Simulation**

Characteristics of an Electrolyte System

- Some molecular species dissociate partially or completely into ions in a liquid solvent
- Liquid phase reactions are always at chemical equilibrium
- Presence of ions in the liquid phase requires non-ideal solution thermodynamics
- Possible salt precipitation
- Some examples include:
  - Solutions with acids, bases or salts
  - Sour water solutions
  - Aqueous amines or hot carbonate for gas sweetening

Types of Components (1)

- Solvents: Standard molecular species
  - Water
  - Methanol
  - Acetic Acid
- Soluble Gases: Henry's Law components
  - Nitrogen
  - Oxygen
  - Carbon Dioxide

Types of Components (2)

- Ions: Species with a charge
  - H_3O^+
  - OH^-
  - Na^+
  - Cl^-
  - $Fe(CN)_6^{3-}$
- Salts: Each precipitated salt is a new pure component
  - NaCl(s)
  - $CaCO_3$(s)
  - $CaSO_4$•$2H_2O$ (gypsum)
  - Na_2CO_3•$NaHCO_3$ •$2H_2O$ (trona)

Apparent and True Components (1)

- True component approach
  - Result reported in terms of the ions, salts and molecular species present after considering solution chemistry
- Apparent component approach
  - Results reported in terms of base components present before considering solution chemistry
  - Ions and precipitated salts cannot be apparent components
  - Specifications must be made in terms of apparent components and not in terms of ions or solid salts
- Results are equivalent

Apparent and True Components (2)

- Example: NaCl in water
  - Solution chemistry
    - $NaCl \rightarrow Na^+ + Cl^-$
    - $Na^+ + Cl^- \leftrightarrow NaCl(s)$
  - Apparent components
    - H_2O, NaCl
  - True components
    - H_2O, Na^+, Cl^-, NaCl(s)

Electrolyte Wizard (1)

- Generates new components (ions and solid salts)
- Revises the Pure component databank search order so that the first databank searched is now ASPENPCD
- Generates reactions among components
- Sets the Property method to ELECNRTL
- Creates a Henry's Component list

Electrolyte Wizard (2)

- Retrieves parameters for:
  - Reaction equilibrium constant values
  - Salt solubility parameters
  - ELECNRTL interaction parameters
  - Henry’s constant correlation parameters
- Generated chemistry can be modified. Simplifying the Chemistry can make the simulation more robust and decrease execution time
- Note: It is the user’s responsibility to ensure that the Chemistry is representative of the actual chemical system

Simplifying the Chemistry

- Typical modifications include:
  - Adding to the list of Henry's components
  - Eliminating irrelevant salt precipitation reactions
  - Eliminating irrelevant species
  - Adding species and/or reactions that are not in the electrolytes expert system database
  - Eliminating irrelevant equilibrium reactions

Electrolyte Demonstration

- Model the treatment of a sulfuric acid waste water stream using lime (Calcium Hydroxide). Use the true component approach

Remove from the chemistry:

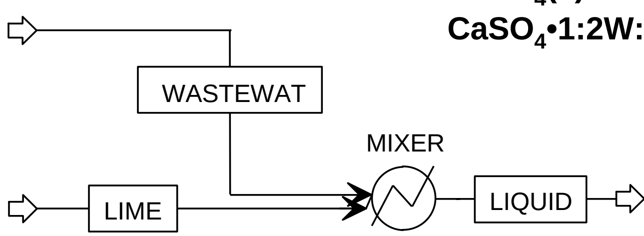
$CaSO_4$(s)

$CaSO_4$•1:2W:A(s)

10 kmol/hr
5 mole% H_2SO_4

Temp = 25°C
Pres = 1 bar

10 kmol/hr
5 mole% $Ca(OH)_2$



When finished, save as filename: ELEC.BKP

Steps for Using Electrolytes

1. Specify the possible apparent components on the Components Specifications Selection sheet
2. Click the Elec Wizard button to generate components and reactions for electrolyte systems. There are four steps:
   1. Define base components and select reaction generation options
   2. Remove any undesired species or reactions from the generated list
   3. Select simulation approach for electrolyte calculations
   4. Review physical properties specifications and modify the generated Henry components list and reactions

Limitations of Electrolytes (1)

- Restrictions using the True component approach:
  - Liquid-liquid equilibrium cannot be calculated
  - The following models may not be used:

• Equilibrium reactors:	RGibbs and REquil
• Kinetic reactors:	RPlug, RCSTR, and RBatch
• Shortcut distillation:	Distl, DSTWU and SCFrac
• Rigorous distillation:	MultiFrac and PetroFrac

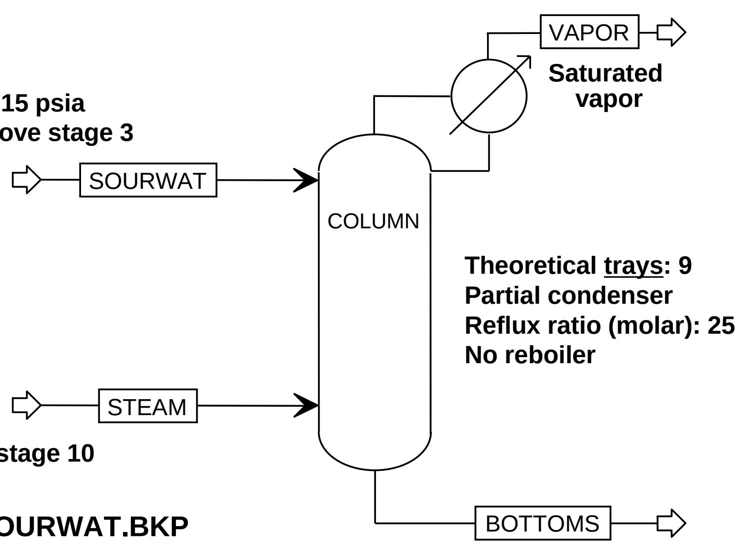
Limitations of Electrolytes (2)

- Restrictions using the Apparent component approach:
  - Chemistry may not contain any volatile species on the right side of the reactions
  - Chemistry for liquid-liquid equilibrium may not contain dissociation reactions
  - Input specification cannot be in terms of ions or solid salts

Electrolytes Workshop (1)

- **Objective: Model a sour water stripper using electrolytes. Use the apparent component approach**

T = 190°F, P = 15 psia
10000 lb/hr above stage 3
99. 7 wt% H_2O
0.1 wt% NH_3
0.1 wt% H_2S
0.1 wt% CO_2



P = 15 psia
Vap. frac = 1
2000 lb/hr on stage 10

Save as: SOURWAT.BKP

Electrolytes Workshop (2)

- Part A
  - Why aren't the ionic species' compositions displayed on the results forms? How can they be added?

- Part B
  - Add a sensitivity analysis
    a. Vary the steam flow rate from 1000-3000 lb/hr and tabulate the ammonia concentration in the bottoms stream
    b. Vary the column reflux ratio from 10-50 and observe the condenser temperature

Electrolytes Workshop (3)

- <u>Part C</u>
  - Create design specifications
    - After hiding the sensitivity blocks, solve the column with two design specifications so that the target ammonia concentration in the bottoms stream is 50 ppm and the target condenser temperature is 190°F
    - Use the boundaries from Part B