think simulation!

Simulating refining overhead chemistry in PRO/II

Using the OLI Mixed-Solvent Electrolyte (MSE) model

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09/15/2016

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OLI and SimSci partnership: two levels

- OLI embedded in PRO/II as PRO/IIe
  - SimSci purchased the OLI model in 1983
  - OLI full support provided for the next 33 years
    - All OLI solver improvements made for the PRO/IIe software as well as for OLI
    - PRO/IIe contains a subset of the components in OLI's AQ (Aqueous) model which is also known as the limited public databank

      All OLI database improvements were also applied for the limited databank when applicable to PRO/II components
- OLI Engine in PRO/II as a joint product with OLI - SimSci
  - Full OLI's AQ model databank
    - An additional capability beyond PRO/IIe limited AQ databank
  - Using the OLI MSE (Mixed Solvent Electrolyte) framework
    - Makes accurate simulation of highly concentrated systems possible

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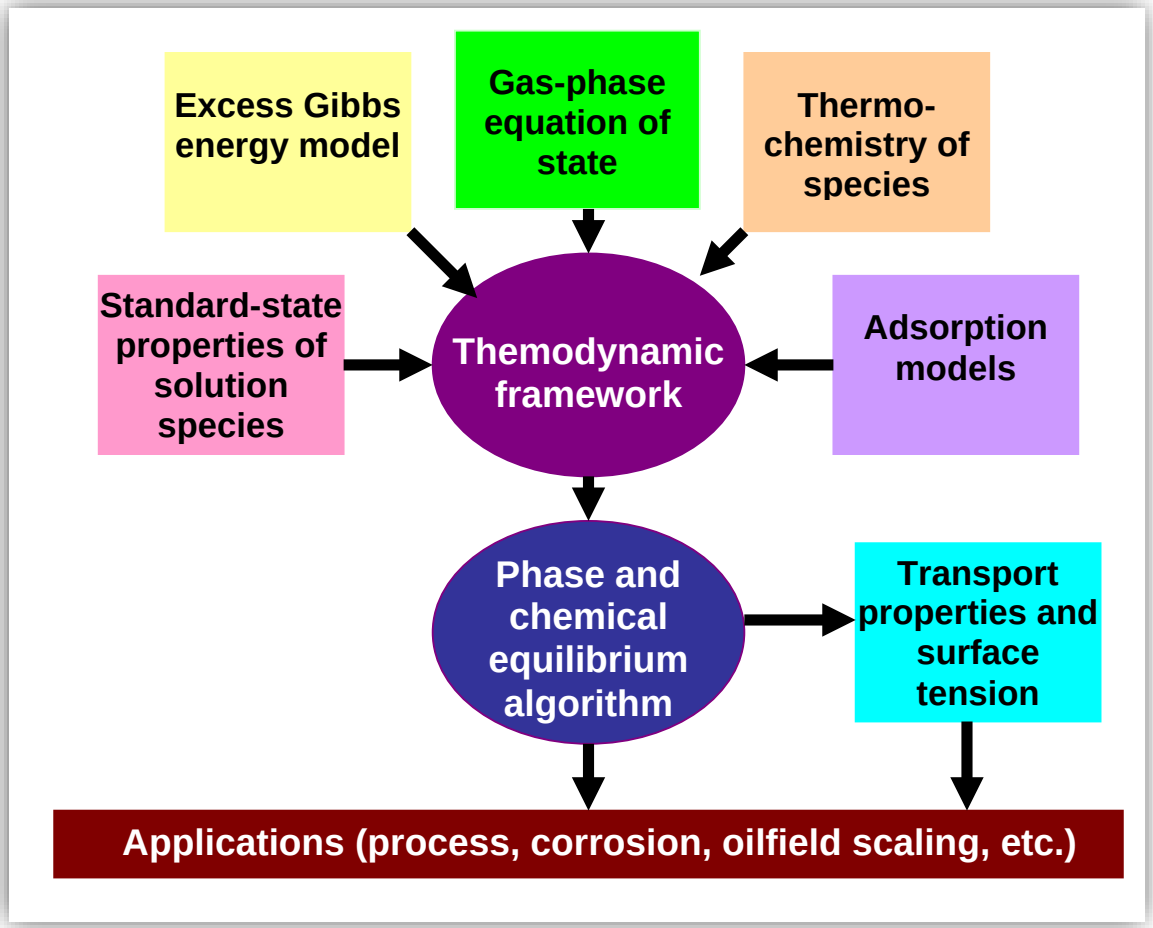
Mixed-solvent electrolyte model(MSE)



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History of OLI Systems and Chemistry in Refinery Overheads

- Prior to this project, the MSE parameters were only available for a limited subset of the chemistry used in these processes.
- The refinery overhead chemistry project involved work on targeted species and their interactions.
- New MSE parameters have now been developed for the pure, binary and multicomponent systems of the targeted species on the basis of various kinds of experimental data.

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Overview of the project report

- Pure components:
  i. 20 amines as specified by the members of the consortium
  ii. Corresponding 20 amine hydrochlorides
- Binary systems:
  i. amines and water
  ii. amines and hydrocarbons
  iii. amine hydrochlorides and water
- Ternary systems:
  i. amines, water and hydrocarbons
  ii. amines water and hydrogen sulfide
  iii. amines, water and carbon dioxide
- Quaternary systems:
  i. amines, water, hydrogen sulfide and carbon dioxide

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Implementation of the refinery overhead project

- An implementation of the parameters in the OLI software (including the Analyzer and alliance products) that makes it possible to perform:
  - Simultaneous phase and chemical equilibrium computations
  - Parametric studies, e.g., simulations of phase changes as the temperature of the stream varies or other conditions are altered
  - Process simulation studies using the OLI Engine in PRO/II.

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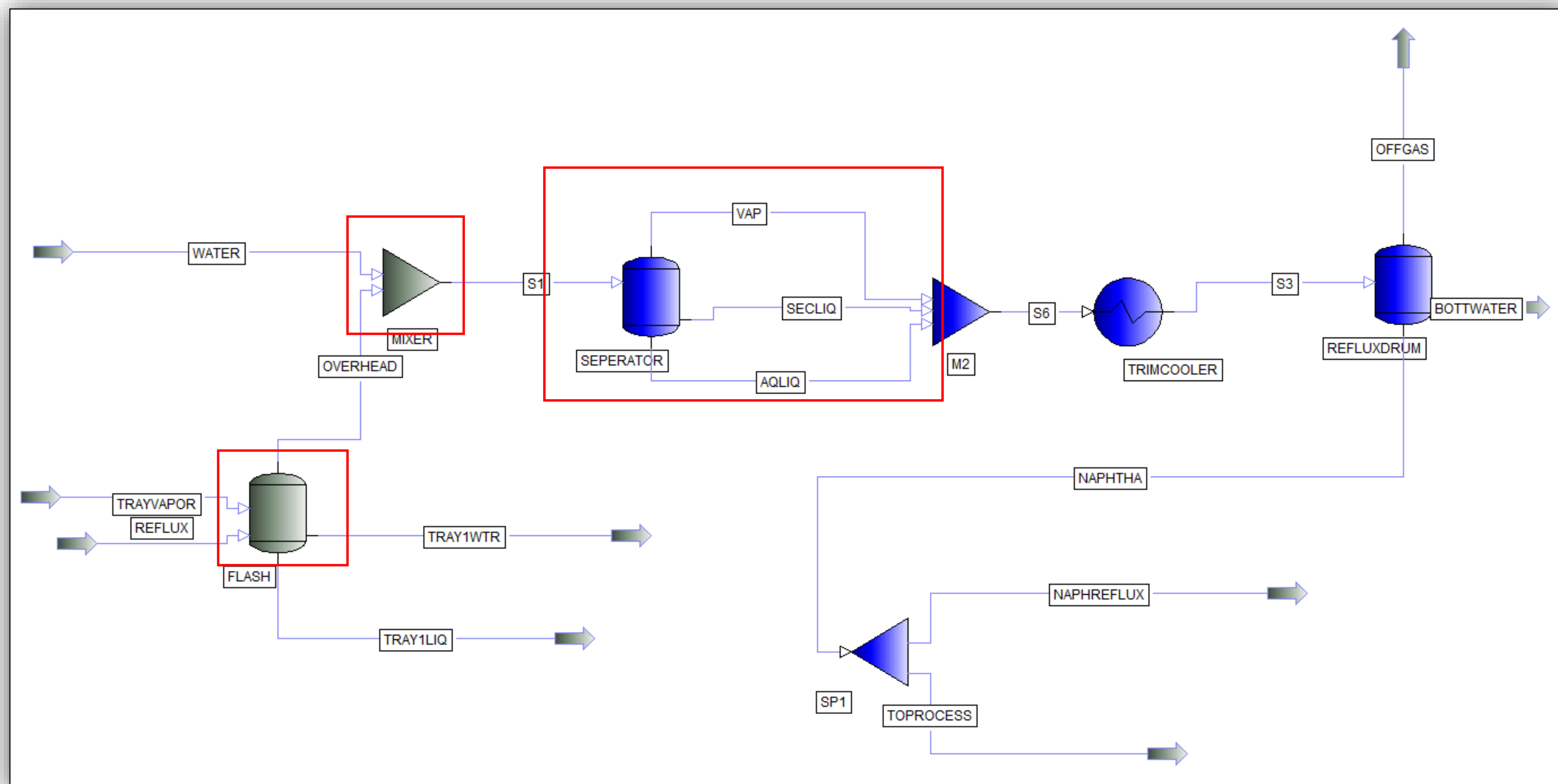
Example of Refinery Overhead Simulation in PRO/II



[illegible] distinct phases to
[illegible] transitions clearly.

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Example of Refinery Overhead Simulation

- The image in the previous slide is representative of a refinery overhead process flow.
- The flash unit is assumed to be the top tray of a crude unit distillation tower.
- The overhead of the tower will go on to a mixer to be mixed with makeup water.
- Purpose of the separator for this simulation was to get three distinct phases to show the phase transitions clearly.

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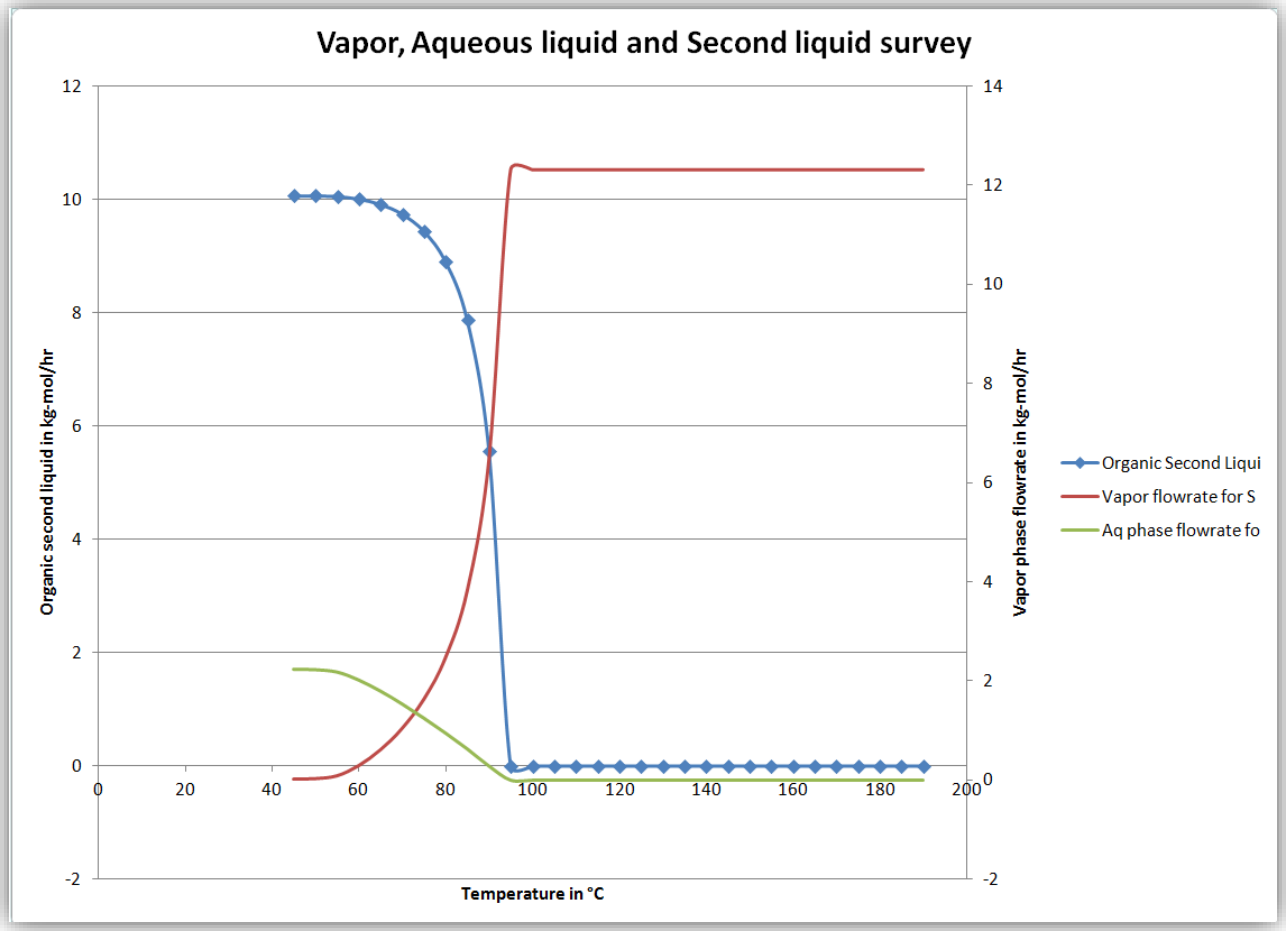
Phase transitions from the separator : Results of PRO/II simulation



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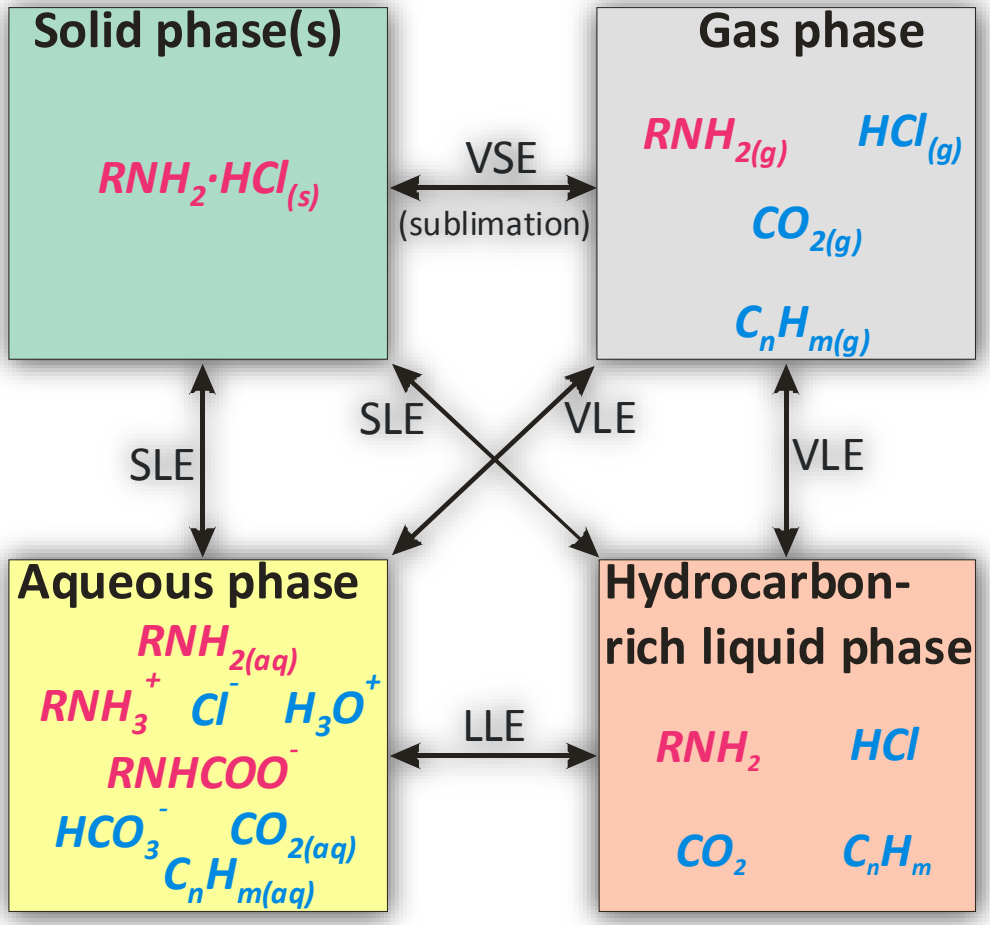
Conceptual scheme of the phases species and phase equilibria for amines



2. Lencka, M. M., Kosinski, J. J., Wang, P., & Anderko, A. (2015, October 17). Thermodynamic modeling of aqueous systems containing amines and amine hydrochlorides: Application to methylamine, morpholine, and morpholine derivatives. *Fluid Phase Equilibria, 418*(2016), 160-174.

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Schematic diagram explanation

- VLE for mixtures of amines with water to predict partitioning of amines between vapor and aqueous phase
- VSE for amine hydrochlorides to determine possibility of precipitation of amine hydrochlorides from the gas phase
- SL and SLV equilibria for amine hydrochlorides in water, to influence transition between solid amine hydrochlorides and concentrated amine hydrochloride solutions (corrosive in nature)
- Speciation in the aqueous phase involving equilibrium between molecular and ionized forms of the amines, dissociation of acid gases and formation of carbamate ions in presence of CO_2
- Partitioning of amines and acid gases between gas phase and hydrocarbon rich phase.

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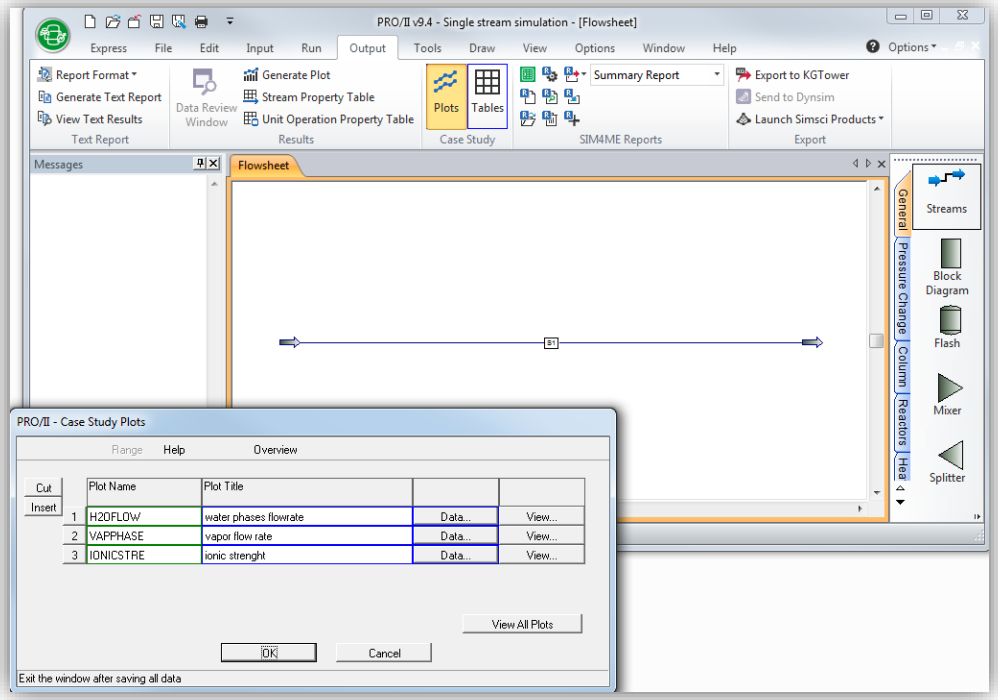
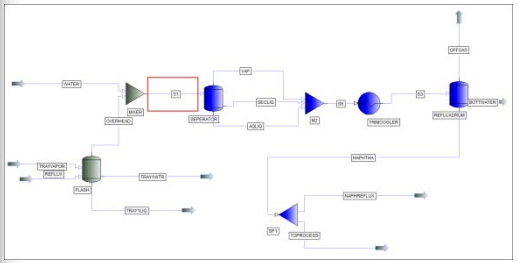
Isolating a single stream for plotting purposes in PRO/II

- The single stream S1 from the overhead refinery simulation was isolated to make plotting easier for three phases.





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VLE flash of the stream

- A quick ‘hot key’ VLE flash 

shows the phase separation for S1.

STREAM 'S1'

	TOTAL	VAPOR	LIQUID 1	LIQUID 2
RATE, LB-MOL/HR	5.3020	3.0346E-03	5.1523	0.1467
TEMPERATURE, F	77.00	77.00	77.00	77.00
PRESSURE, PSIA	33.70	33.70	33.70	33.70
MOLECULAR WEIGHT	99.2469	12.8002	101.6096	18.0553
FRACTION		5.7236E-04	0.9718	0.0277
ENTHALPY, BTU/LB-MOL	-94207.2808	-11773.7787	-93441.1555	-122819.5723
CP, BTU/LB-F	0.4873	0.7490	0.4847	0.9951
MOLAR FLOWRATES, LB-MOL/HR				
1 - H2O	0.1477	4.1835E-05	1.1675E-03	0.1465
2 - C2H6	4.1888E-03	2.1092E-05	4.1676E-03	7.8105E-08
3 - C3H8	1.7637E-03	3.0886E-06	1.7606E-03	9.5581E-09
4 - C4H10	1.5432E-03	8.3962E-07	1.5424E-03	2.2321E-09
5 - CH4	5.7320E-03	2.5378E-04	5.4775E-03	7.1720E-07
6 - AS1_286K	0.7665	2.8369E-04	0.7662	2.4740E-08
7 - AS1_338K	1.7839	1.0994E-04	1.7838	3.0136E-09
8 - AS1_389K	1.3187	1.1064E-05	1.3187	1.1106E-10
9 - AS1_440K	0.9842	8.4792E-07	0.9842	4.1679E-12
10 - AS1_493K	0.2836	1.2032E-08	0.2836	5.9020E-14
11 - H2S	1.7637E-03	7.5866E-06	1.6646E-03	9.1497E-05
12 - H2	2.4251E-03	2.3009E-03	1.2060E-04	3.6180E-06
13 - HCL	1.5432E-06	6.8666E-22	0.0000	1.5432E-06
14 - MEXH	1.1023E-04	8.9290E-12	7.4051E-06	1.0283E-04
15 - AS1	0.0000	0.0000	0.0000	0.0000
16 - HCL.1H2O	0.0000	0.0000	0.0000	0.0000
17 - HCL.2H2O	0.0000	0.0000	0.0000	0.0000

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Water dew point, ionic dew point and salt point definitions

- Water dew point is defined as the temperature where the liquid water first appears.[1]
- Ionic dew point represents the first drop of liquid formed as a consequence of ionic attraction and partial pressures of the three components.[1]
- Salt point is the temperature at which a dry or crystalline salt forms due to higher partial pressure of the salt components. [1]

1. Armistead/Wills, K., Leslie, D., & Strong, R. (n.d.). Crude Unit Overhead Corrosion Control Successfully Driven by Ionic Modeling. *STG34NACE2015*. Paper 6010

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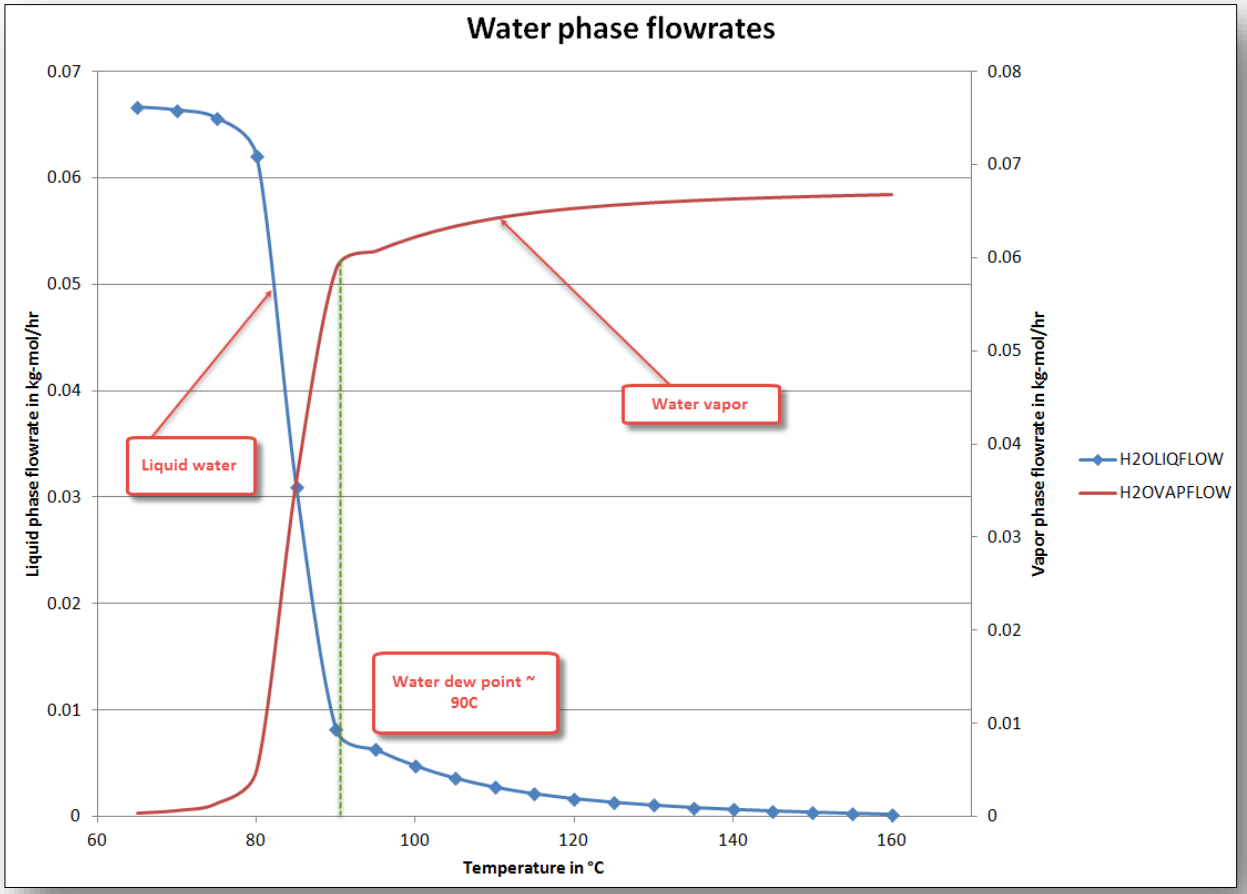
Water dew point from PRO/II simulation (plotted using Excel)



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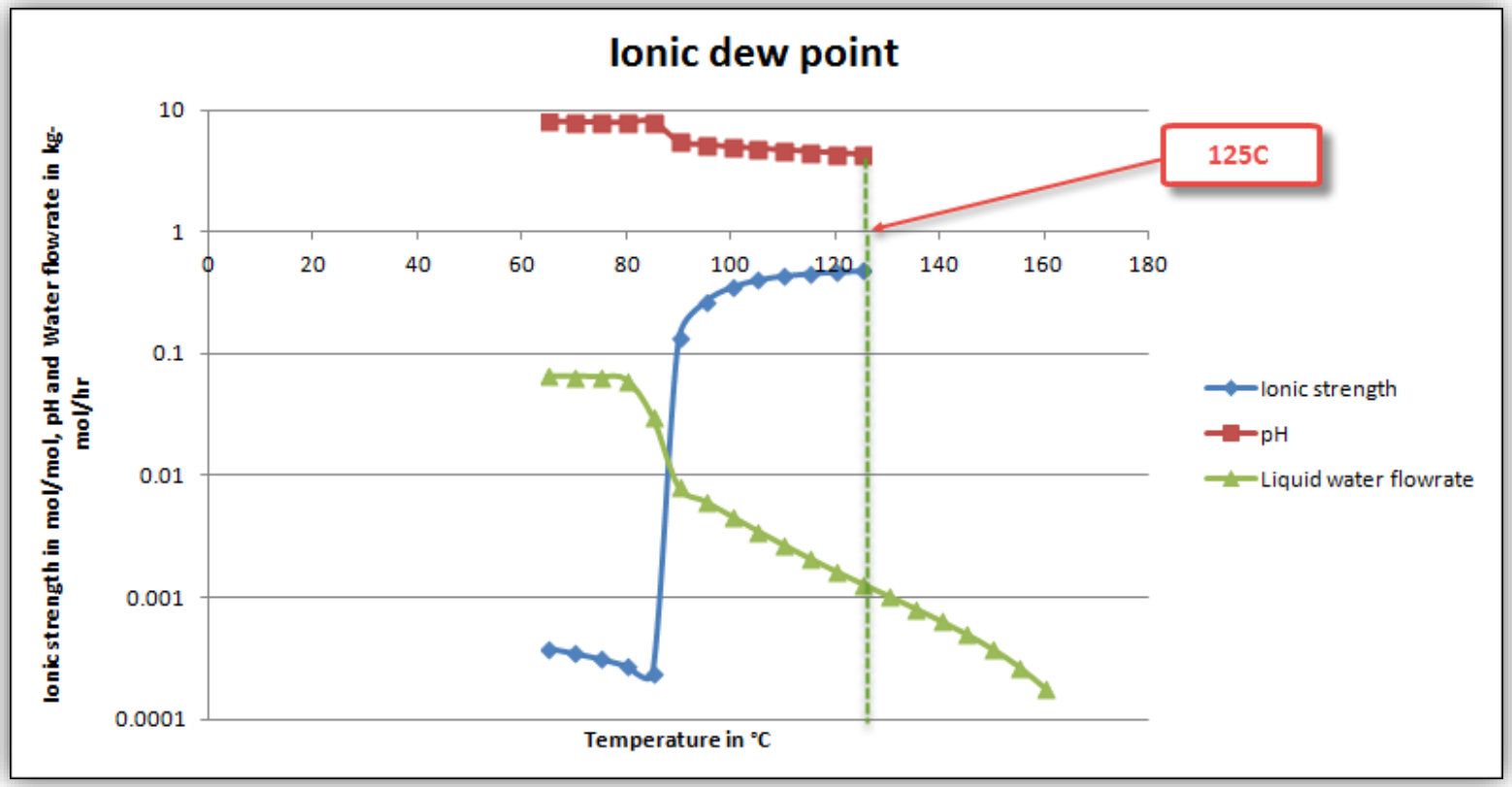
Ionic dew point from PRO/II simulation (plotted using Excel)



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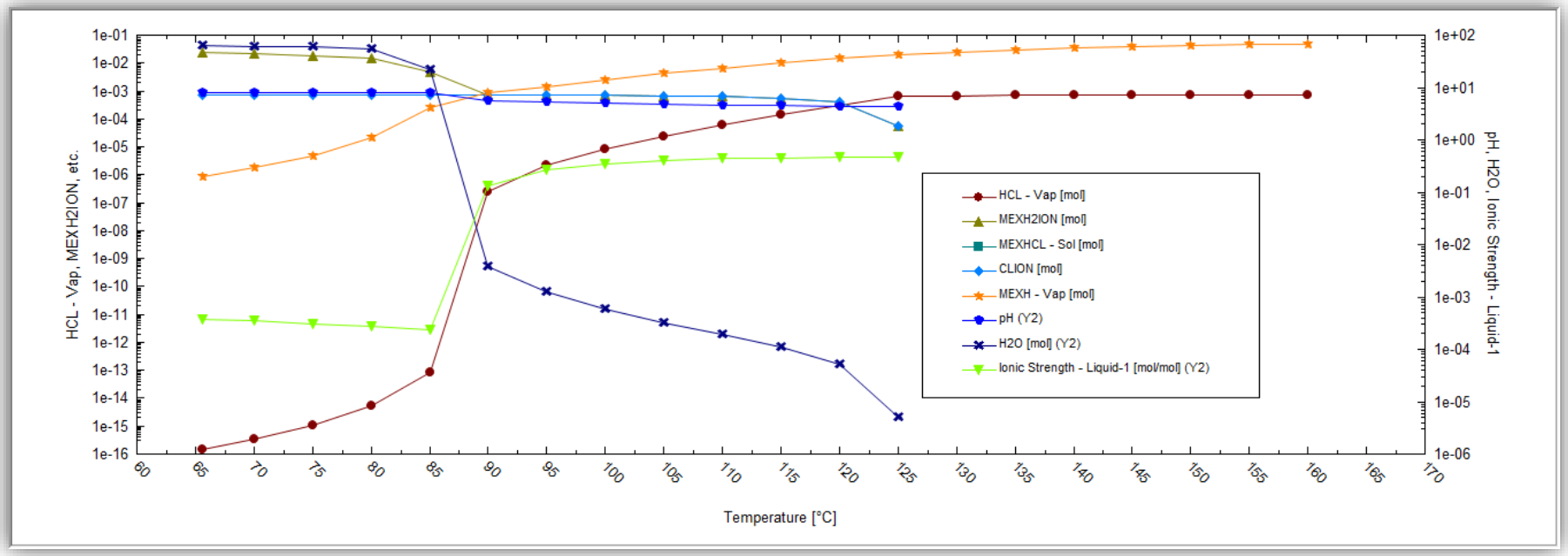
OLI Studio for the chemistry



MEXH in this slide refers to the Ethanolamine or 2-Aminoethanol. MEXH is the OLI tag name for the component

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Interpretation of simulation results

- In the following plot, the amine MEXH does not form a solid phase
- Below 85°C, we observe high concentrations of amine-H^+ and Cl^- ions in the liquid 1 phase (L1)
- The concentrations of the ions are superimposed on the water concentrations of L1 and L2 phases
- This indicates the initial formation of the aqueous phase corresponding with a high ion concentration in this phase

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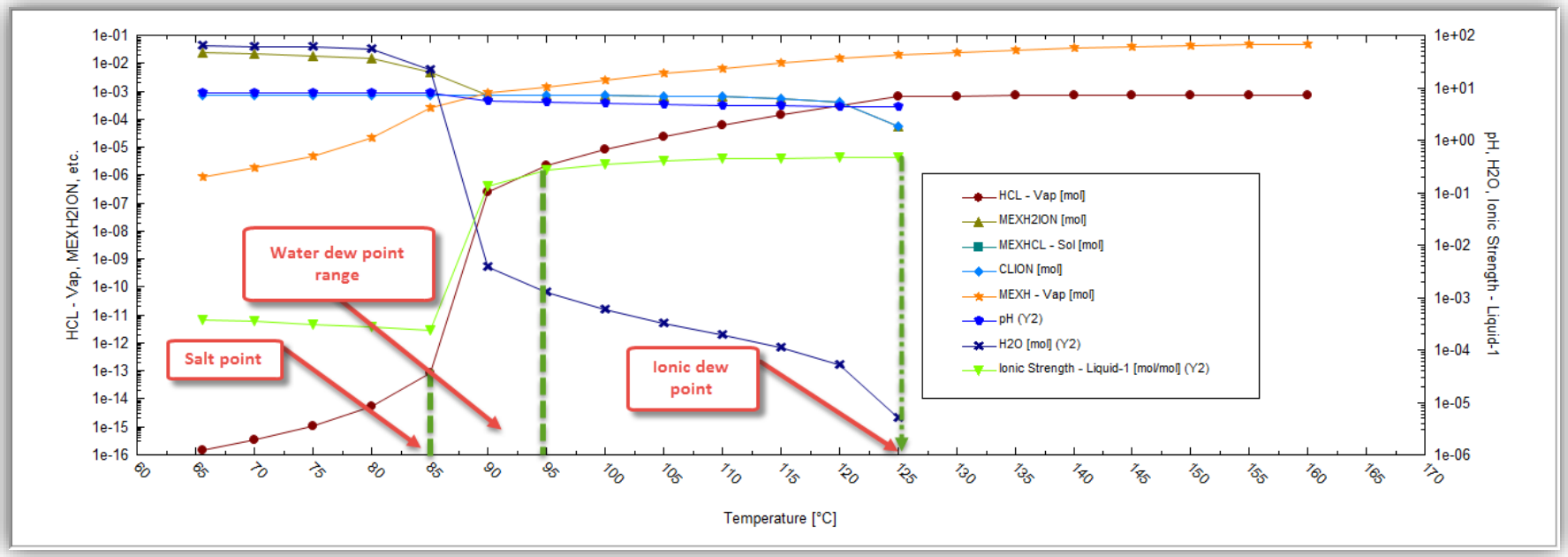
Identifying salt point, water dew point and ionic dew point in Studio



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Salt point

- The formation of a concentrated solution of ions should be identified as the separation of a liquid salt .
- It should be noted that the liquid salt will practically never be pure because the ionic amine hydrochloride liquids are freely miscible with water.
- The above statement makes the identification of Ionic dew point even more important.

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Salt Point with Studio

- Since MEXH-HCL solid does not form, we will look at the concentrations of amine ions and chloride ions in OLI Studio.
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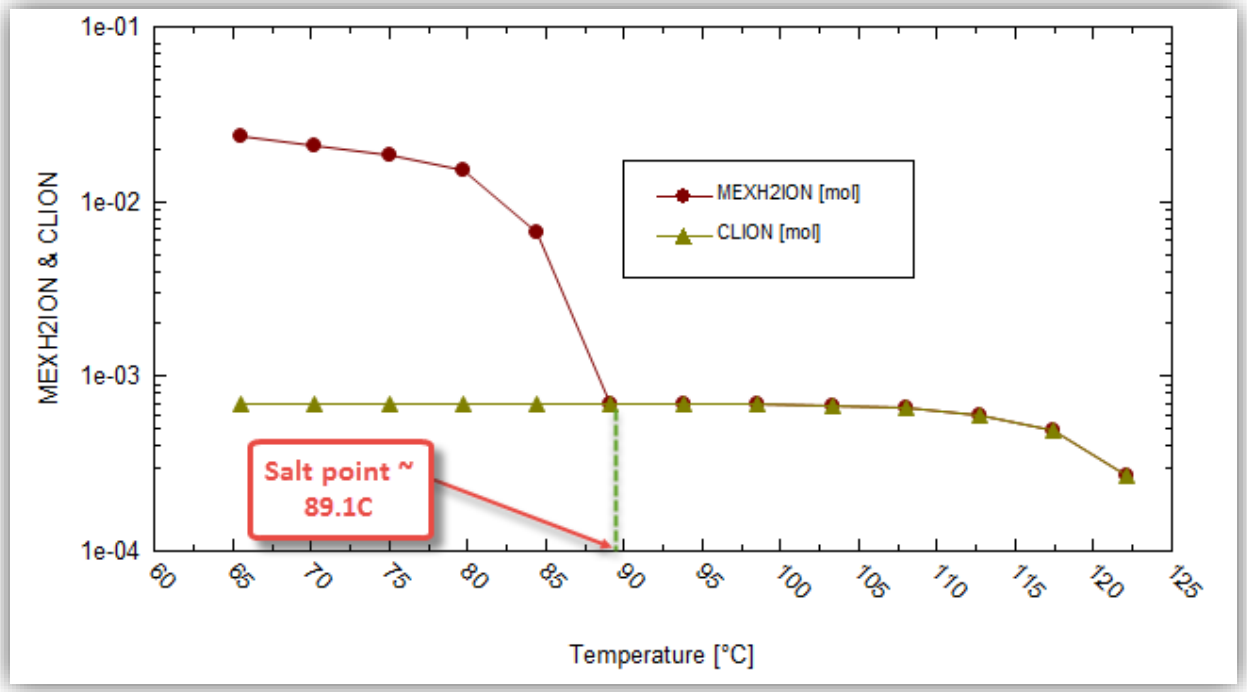

MEXH2ION in this slide refers to the Hydrogen 2-Aminoethanol (+1) ion. MEXH is the OLI tag name for the component ethanolamine.

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Future work

- OLI Chemistry in Refining Overheads II meeting
  - 20th September 2016 via web
  - Validation of some estimation work / possible new amines
- Presentation at OLI Simulation Conference
  - 25-26 October 2016 in NJ USA
  - Total study on comparing model to refinery situation
- Simulation study with other amines will be performed in PRO/II with and without a distillation column
  - Phase separations will be identified more thoroughly for this project
  - A solid forming amine will be used to create the study

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References

1. Armistead/Wills, K., Leslie, D., & Strong, R. (n.d.). Crude Unit Overhead Corrosion Control Successfully Driven by Ionic Modeling. *STG34NACE2015*. Paper 6010
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Thank you

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Questions?

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Resources available

- OLI Proposal or webex link to the meeting
- Simulation conference information
- Evaluation copies of OLI Engine in PRO/II
- Sample work-up of your application

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