

# Modeling and Computation of Thermodynamic Equilibrium for Mixtures of Inorganic and Organic Species

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# Motivations

Development of a thermodynamic model for mixed inorganic-organic atmospheric aerosols for the prediction of thermodynamic equilibria, phase separation, and gas/particle partitioning (UHAERO).

- Various thermodynamic modules for inorganic aerosols (ISOROPPIA, SCAPE2, GFEMN, AIM2, ADDEM, EQSAM, etc.)
- Thermodynamic modules for pure organic-containing aerosols (*phase lock* between hydrophilic and hydrophobic organic components).
- The presence of organic species influences phase transitions of the deliquescence and efflorescence of salts (*salt-in - salt-out effect*). Reciprocally, dissolved electrolytes have effects on the solubility of organic components.



# Outline

- Thermodynamics of aerosols containing inorganic electrolytes and dicarboxylic acids
  - Modeling and activity coefficients.
  - Computational issues.
  - Construction of phase diagrams.
- Thermodynamics of aerosols containing inorganic electrolytes and organic compounds
  - Modeling of phase separation and chemical reactions.
  - Modeling Issues
  - Construction of phase diagrams.



# Modeling the Thermodynamics

$$\min \quad G(\mathbf{n}_l, \mathbf{n}_s, \mathbf{n}_g) = \mathbf{n}_g^T \boldsymbol{\mu}_g + \mathbf{n}_l^T \boldsymbol{\mu}_l + \mathbf{n}_s^T \boldsymbol{\mu}_s \quad \leftarrow \text{Gibbs free energy}$$

$$\text{s. t.} \quad \mathbf{A}_g \mathbf{n}_g + \mathbf{A}_l \mathbf{n}_l + \mathbf{A}_s \mathbf{n}_s = \mathbf{b}, \quad \leftarrow \text{Stoichiometry}$$

$$\mathbf{n}_g > \mathbf{0}, \quad \mathbf{n}_l > \mathbf{0}, \quad \mathbf{n}_s \geq \mathbf{0} \quad \leftarrow \text{Positive concentrations}$$

where

- $\mathbf{n}_\alpha, \alpha = l, g, s$  are the concentrations of species in the liquid phase, gas phase, and the solid states respectively
- $\boldsymbol{\mu}_\alpha, \alpha = l, g, s$  are the chemical potentials.
- $\mathbf{A}_\alpha, \alpha = l, g, s$  are the stoichiometry matrices.



# Modeling the Activity Coefficients

- The chemical potential vectors are given by

$$\mu_g = \mu_g^0 + \mathcal{R}T \ln a_g,$$

$$\mu_l = \mu_l^0 + \mathcal{R}T \ln a_l,$$

$$\mu_s = \mu_s^0,$$

where  $\mu_\alpha^0$  is a constant chemical potential and  $a_\alpha$  is the *activity function*.

- The **PSC model** (Clegg *et al.*, 1998) or the **ExUNIQUAC model** (Thomsen, Rasmussen, 1999) are used to describe the activity coefficients for pure inorganic compounds.
- The **UNIFAC model** (Fredenslund, Gmehling, Rasmussen, 1979 & 1982) is used to describe the activity coefficients for organic compounds.



# Modeling Dicarboxylic Acids

- Addition of dicarboxylic acids increases the number of components in the liquid and gas phases.
- **Modification of the stoichiometry:**



- **Modification of the activity coefficient model** with the CSB hybrid model (*Clegg and Seinfeld, 2006*). Introduction of molal activity coefficients of an ion ( $\gamma_i$ ) and an uncharged organic solute ( $\gamma_n$ ) in the liquid mixture:

$$\ln(\gamma_i) = \Delta \ln(\gamma_i[\text{ion-water}]) + \Delta \ln(\gamma_i[\text{ion-organic}]),$$

$$\ln(\gamma_n) = \Delta \ln(\gamma_n[\text{organic-water}]) + \Delta \ln(\gamma_n[\text{ion-organic}]).$$



# Modeling Interactions and Organic Salts

- Owing to the lack of data, the interactions between electrolytes and dissociated acids and water respectively are simplified (e.g. organic ions reacts only with positive inorganic ions, organic ions do not interact with each other, etc.)
- **Set of possible organic salts** to be inserted in the model is defined by the activity coefficient model.

*Example:* For the succinic acid, we consider either

- $\text{H}_2\text{Succ}(s)$  (one organic salt).

or

- $\text{H}_2\text{Succ}(s)$ ,  $\text{NH}_4\text{HSucc}(s)$  and  $(\text{NH}_4)_2\text{Succ} \cdot \text{H}_2\text{O}(s)$  (three organic salts).



# Computational Issues

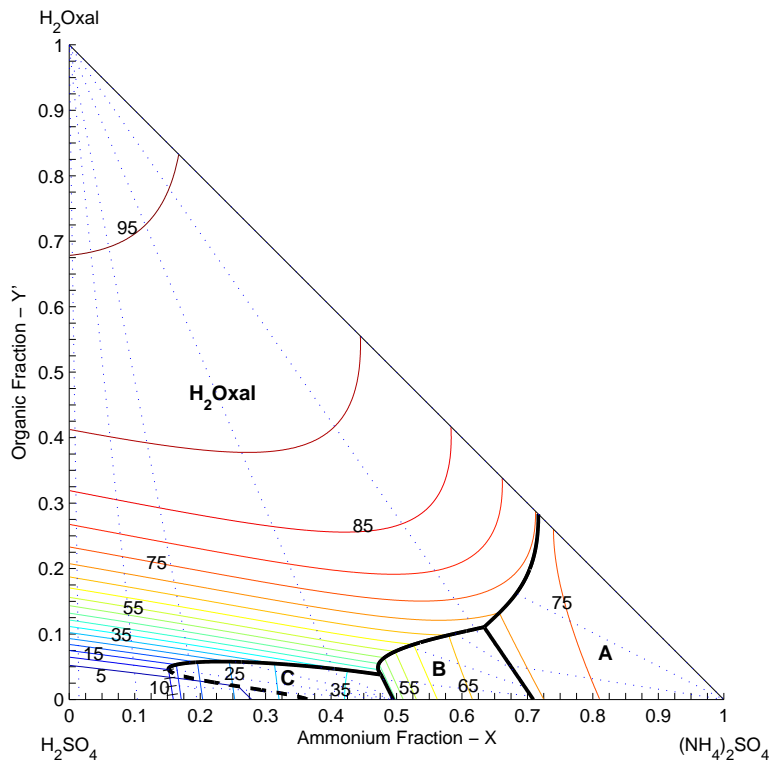
- Accuracy of the computations = Accuracy of the Energy model
  - Error due to the numerics is the rounding error.
  - No a priori information on the equilibrium state.
- Cost of the Computation = Cost of the Energy model evaluation + Cost of the numerics
  - Determination of the thermodynamic equilibrium with a **primal-dual active sets method**, with a *Newton's method* applied to the *KKT system of equations*.
- Flexibility of the Method (Black-Box Algorithm)
  - User-friendly web interface and open-source software.



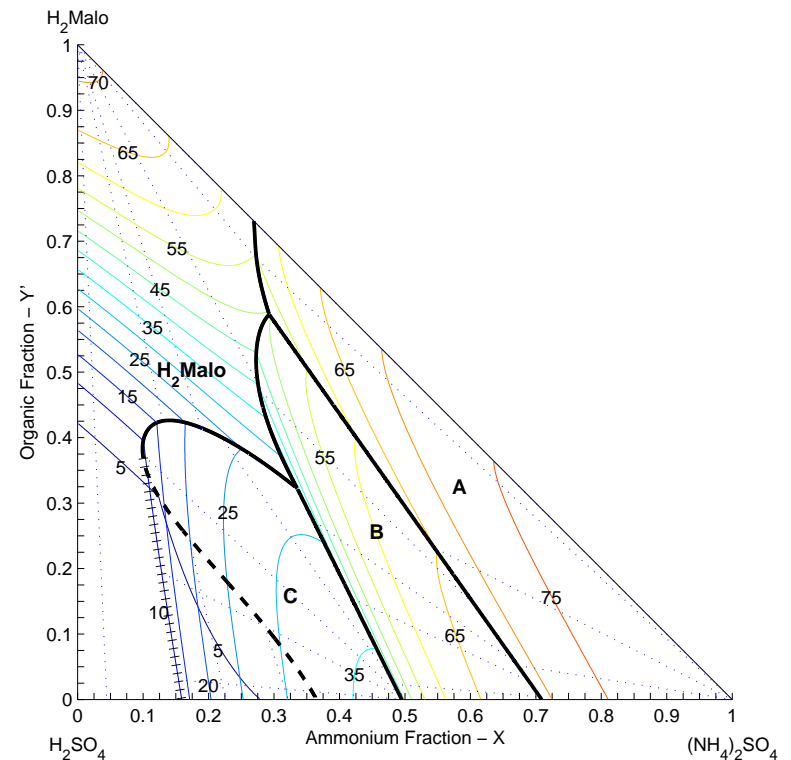
# Sulfate/Ammonium/Acid System

- Thermodynamics of particles with sulfate, ammonium and one dicarboxylic acid (oxalic, malonic, malic, glutaric, maleic, etc.)

## Oxalic acid



## Malonic acid



(A=ammonium sulfate, B=letovicite, C=ammonium bisulfate)

# Computational Efficiency

Sulfate/Ammonium/Acid System with PSC/UNIFAC/CSB model:

	Inorganic + acids	Inorganics only
# Newton it. (avg)	3.5	3.0
CPU time per it. (avg) [ $\mu$ s]	49	24.7
Total CPU per run. (avg) [ $\mu$ s]	171.5	74.1
% for activity coeff. calc.	75 %	64.3 %

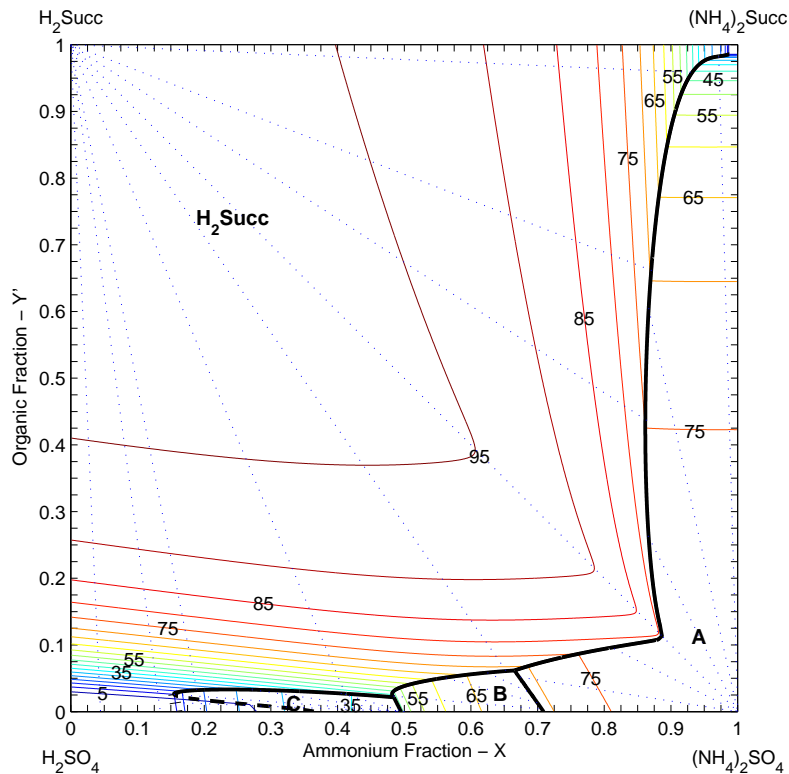
- The computational effort required to calculate the equilibrium state is small compared to the calculation of the activity coefficients.
- The additional computational effort to incorporate the organic components (with respect to inorganics only) does not change the number of iterations but the cost of each iteration.



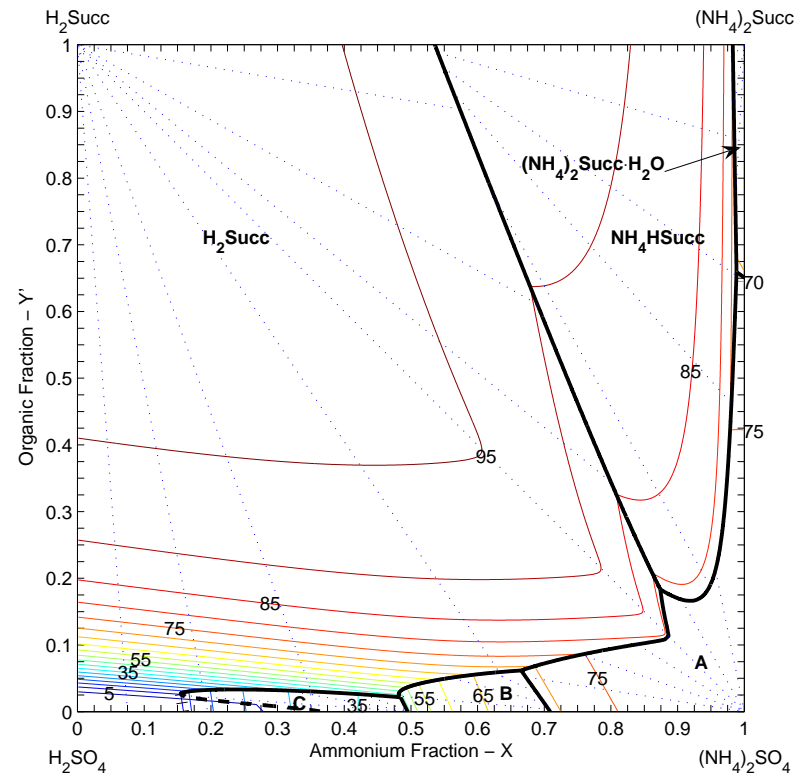
# Succinic Acid

- Sets of potential organic salts in the model:

## $H_2Succ(s)$ only



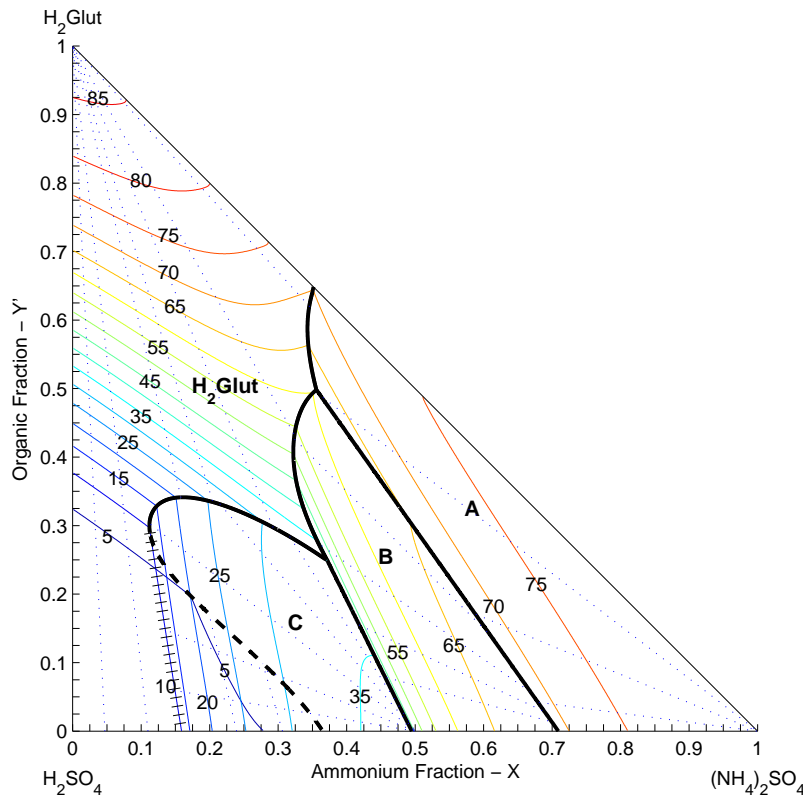
## $H_2Succ(s)$ , $NH_4HSucc(s)$ and $(NH_4)_2Succ \cdot H_2O(s)$



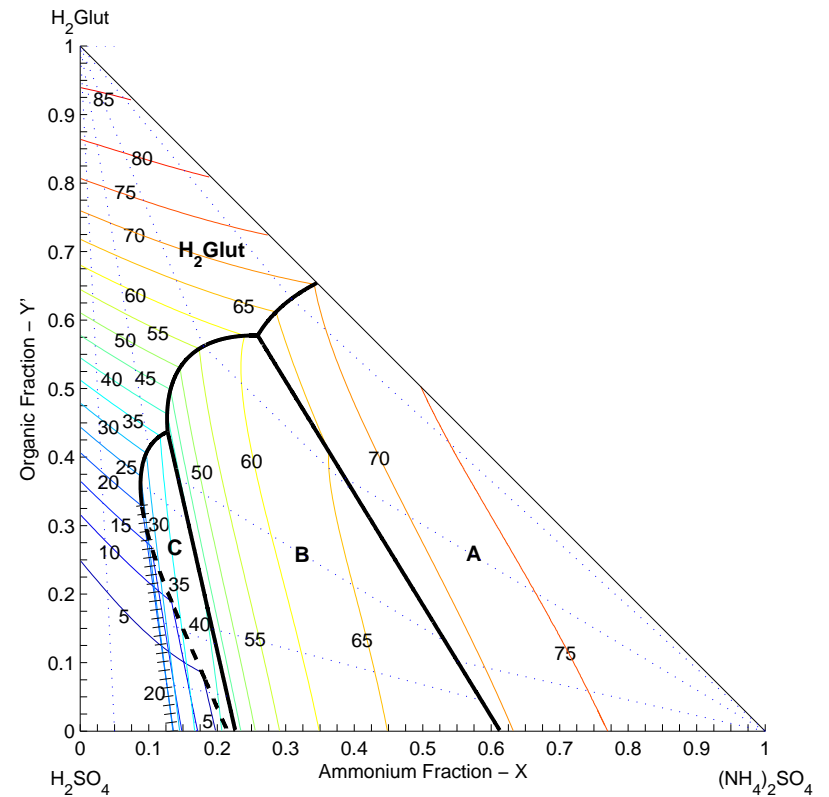
# Sensitivity Analysis

- PSC vs ExUNIQUAC for the activity coefficient model for inorganic electrolytes (sulfate/ammonium system with glutaric acid):

## PSC/UNIFAC/CSB



## ExUNIQUAC/UNIFAC/CSB



# Mixtures of Inorganic and Organic Aerosols

- Phase separation and chemical reactions, salt crystallization and dissociation of electrolytes in **each liquid phase**.
- Complex activity coefficients models (PSC+UNIFAC+coupling).

$$\min \underbrace{\sum_{\alpha=1}^P g(\mathbf{n}_\alpha)}_{\text{non-react. organics}} + \underbrace{\mathbf{n}_{l,w}^T \boldsymbol{\mu}_{l,w}}_{\text{electrolytes in aqueous}} + \underbrace{\mathbf{n}_{l,i}^T \boldsymbol{\mu}_{l,i}}_{\text{electrolytes in all phases}} + \mathbf{n}_g^T \boldsymbol{\mu}_g + \mathbf{n}_s^T \boldsymbol{\mu}_s$$

$$\text{s. t. } \sum_{\alpha=1}^P \mathbf{n}_\alpha = \begin{pmatrix} \mathbf{n}_{l,w} \\ \mathbf{b}_O \end{pmatrix} \quad \text{Mass conservation among liquid phases}$$

$$\mathbf{A}_g \mathbf{n}_g + \mathbf{A}_{l,i} \mathbf{n}_{l,i} + \mathbf{A}_{l,w} \mathbf{n}_{l,w} + \mathbf{A}_s \mathbf{n}_s = \mathbf{b}_I, \quad \text{Stoichiometry relation}$$

$$\mathbf{n}_{l,i}, \mathbf{n}_{l,w}, \mathbf{n}_g > \mathbf{0}, \quad \mathbf{n}_s \geq \mathbf{0}, \mathbf{n}_\alpha \geq \mathbf{0}, \quad \alpha = 1, \dots, P.$$

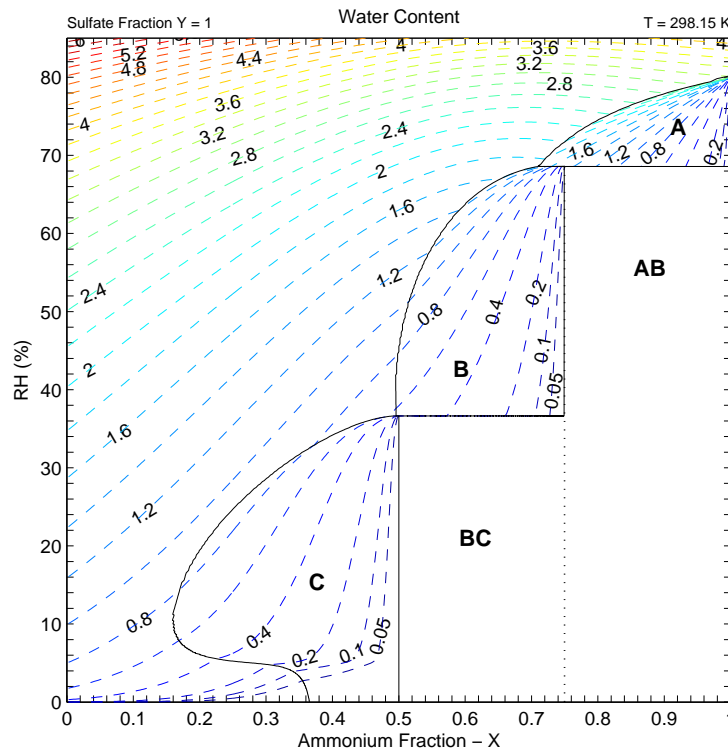
- Inorganic electrolytes only in aqueous phase.



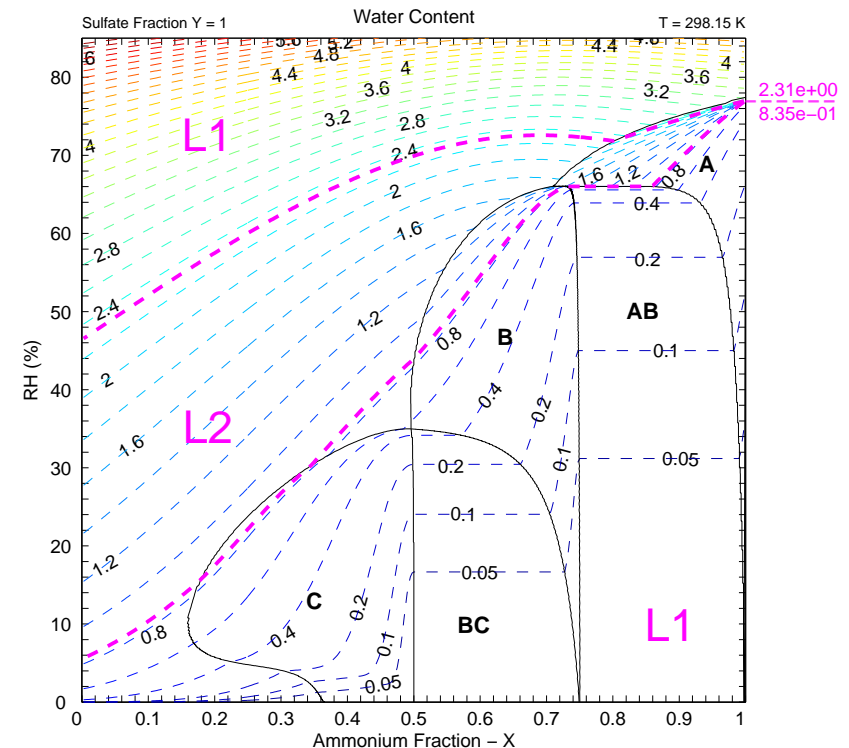
# Sulfate/Nitrate/Ammonium with Organics

- Construction of the phase diagram for the system  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{NH}_4\text{NO}_3/\text{HNO}_3/\text{H}_2\text{O}$  when the system also include two organic species.

without organics



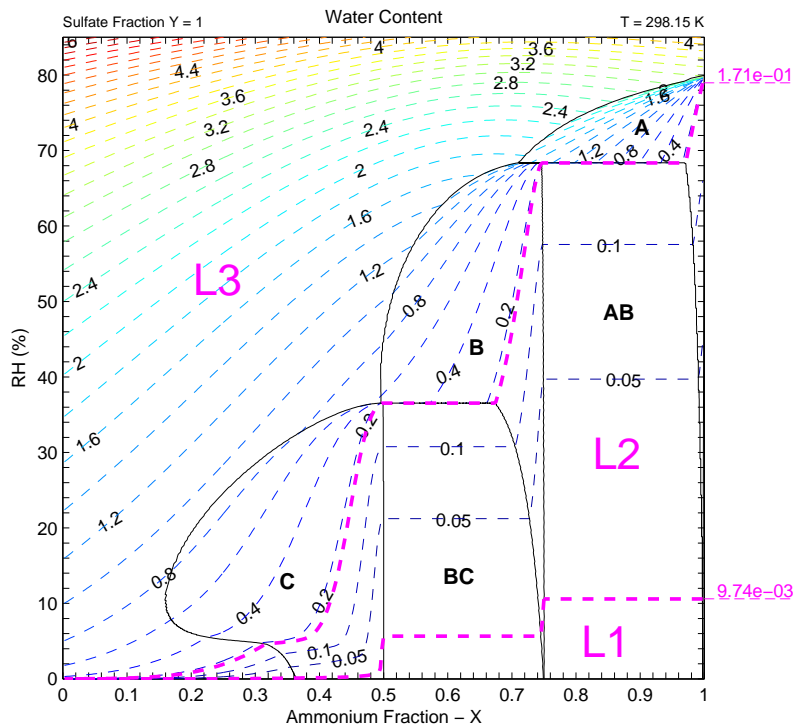
adipic acid/glutaraldehyde



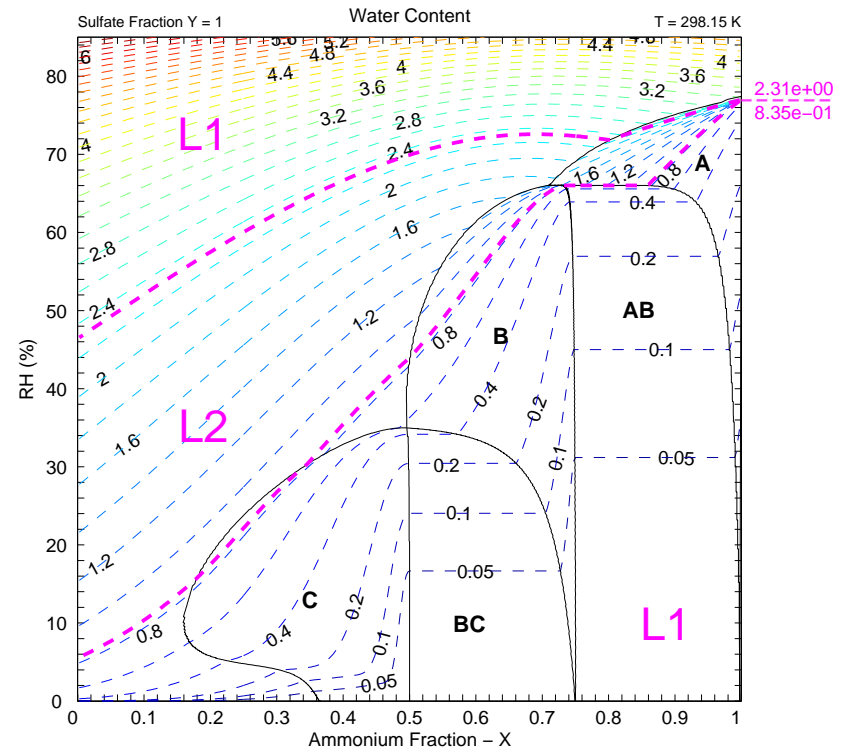
# Sulfate/Nitrate/Ammonium with Organics

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## 1-hexacosanol/pinic acid



## adipic acid/glutaraldehyde



# Conclusions

- Significant impact of organics in inorganic/organic mixtures on crystallization.
- Modeling of activity coefficients with various models (PSC, UNIFAC, CSB, etc.) is still a difficult task.
- Framework is accurate, efficient and flexible.
- **Acknowledgements:** Simon Clegg, University of East Anglia, UK.



<http://aero.math.uh.edu>



## References:

- Amundson et al, Atmos. Chem. Phys.*, 6, 2006 (pure inorganics)
- Amundson et al, J. Geophys. Res.*, to appear, 2007 (dicarboxylic acids)
- Amundson et al, Atmos. Chem. Phys.*, 7, 2007 (pure organics+some mixtures)

