Statistical Mechanics of Multilayer Sorption: Solutions and Surfaces

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Need comprehensive physical chemical description of solutions
- Encompassing the Aerosol **Bulk** and its **Surface**

To describe the composition dependence of
- Nucleation
- Growth to CCN
- Activation to Droplets
- Surface Concentrations – Surface Chemistry
- Phase Partitioning

Ultimately a Gibbs free energy description of the bulk and surface

Statistical Mechanics of Multilayer Sorption: Solutions and Surfaces

Dutcher, Ge, Clegg and Wexler, JPC 2011, 2012, 2013

$$m_j^{o'} = \frac{\left(\dfrac{1-a_w K_w^{DH}}{M_w r_j a_w K_w^{DH}}\right)\left(1-\sum_{i=1}^{n_j-1}\left(\left(a_w K_w^{DH}\right)^i\left(1-C_{j,i}\right)\prod_{k=1}^{i-1}C_{j,k}\right)\right)}{\left(1-a_w K_w^{DH}\right)^2\sum_{p=1}^{n_j-2}\left(p\left(a_w K_w^{DH}\right)^{p-1}\prod_{k=1}^{p}C_{j,k}\right)+\left(\left(n_j-1\right)-\left(n_j-2\right)a_w K_w^{DH}\right)\left(a_w K_w^{DH}\right)^{n_j-2}\prod_{k=1}^{n_j-1}C_{j,k}}$$

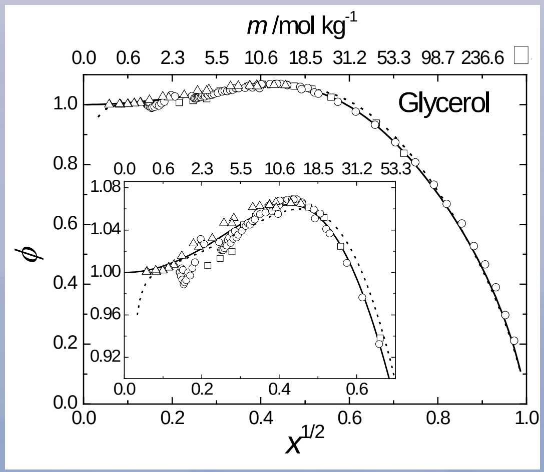
$$a_j^{o'} = \left(K_j^{DH}\right)\left(\left(1-a_w K_w^{DH}\right)\Big/\left(1-\sum_{i=1}^{n_j-1}\left(\left(a_w K_w^{DH}\right)^i\left(1-C_{j,i}\right)\prod_{k=1}^{i-1}C_{j,k}\right)\right)\right)^{r_j}$$

$$\sum_j \frac{m_j}{m_j^{o'}} = 1 \qquad a_j = x_j^* a_j^{o'}$$

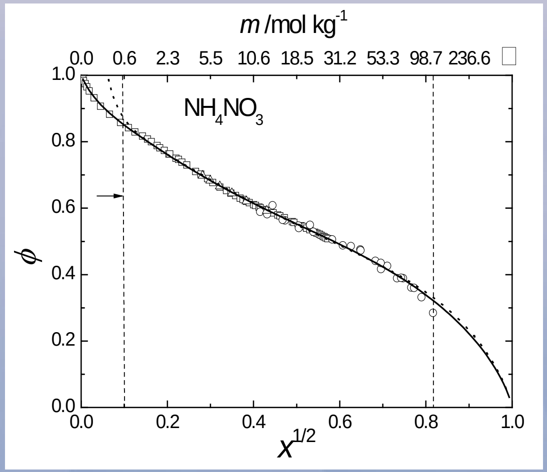
$$\sigma(a_A) = \sigma_W + \frac{kT}{r_A S_W}\ln\frac{1-K_A a_A}{1-K_A a_A(1-C_1)}$$ (In preparation)

Examples

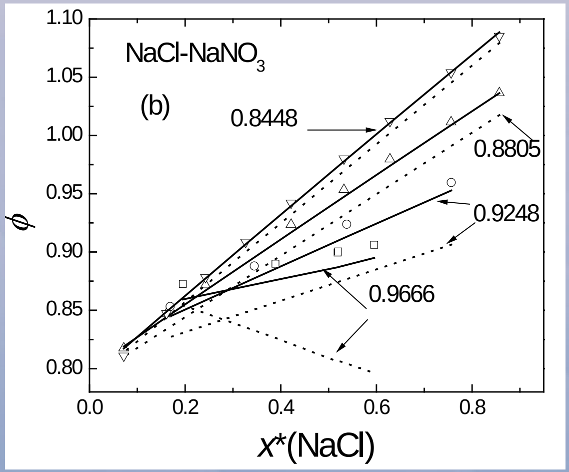
Solution Osmotic Coefficient



Glycerol in water

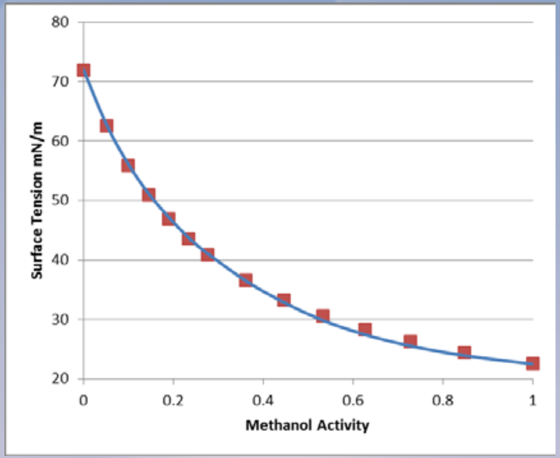


Ammonium Nitrate in water

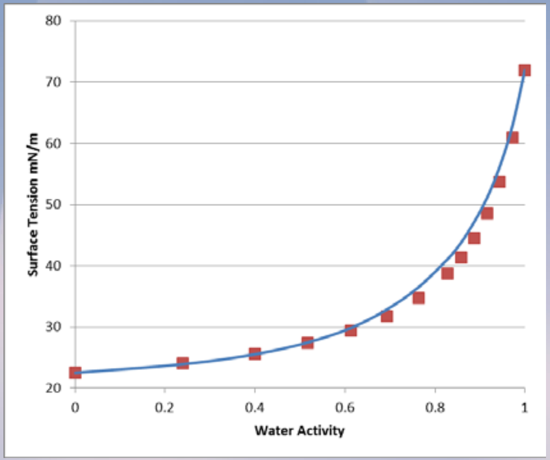


$NaCl-NaNO_3-H_2O$

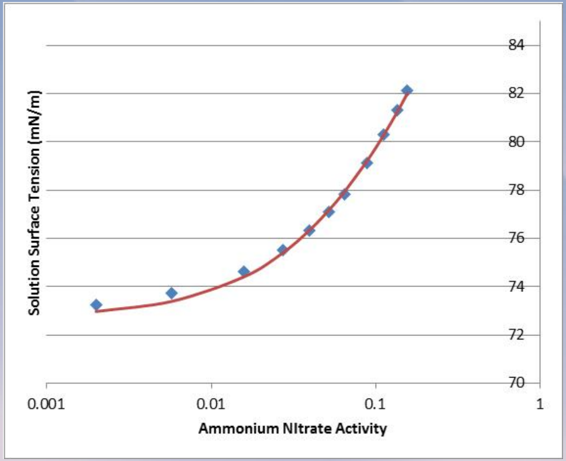
Surface Tension



Methanol in water



Water in methanol



Ammonium Nitrate in water

Statistical Mechanics of Multilayer Sorption: Solutions and Surfaces

Future Directions

Solutions: Future Directions
- Temperature Dependence
- Ion Association e.g., Sulfuric Acid
- Represent Parameters as Functions of Solute & Solvent Properties

Surface Tension: Future Directions
- Temperature Dependence
- Represent Parameters as Functions of Solute & Solvent Properties
- Develop Theory for Multicomponent Solutions/Surfaces

Arbitrary Moment Modeling of Aerosol Size Distribution

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Need arbitrary moment model to capture
- Number for small particle sizes
- Mass for large particle sizes
- Radiation interaction for intermediate sizes

Arbitrary Moment Condensation/Evaporation Equation (Grits and Wexler, 2008)

$$\frac{\partial q_i}{\partial t} = H_i q + H_f q_i - \frac{1}{3}\frac{\partial (H q_i)}{\partial \mu}$$

$$H_f \equiv \frac{1}{f}\left[\frac{\partial f}{\partial t} + \frac{H}{3}\frac{\partial f}{\partial \mu}\right],$$

q_i - concentration of i
q - total concentration
H_i - condensation rate of i
H - total condensation rate
f - size-dependent moment

Arbitrary Moment Modeling of Aerosol Size Distribution

Future Directions

Coagulation Terms for Small Particles
Numerical Methods to Solve Coagulation
Integrate into Process Models (MOSAIC) and Test
Integrate into Climate Models and Test