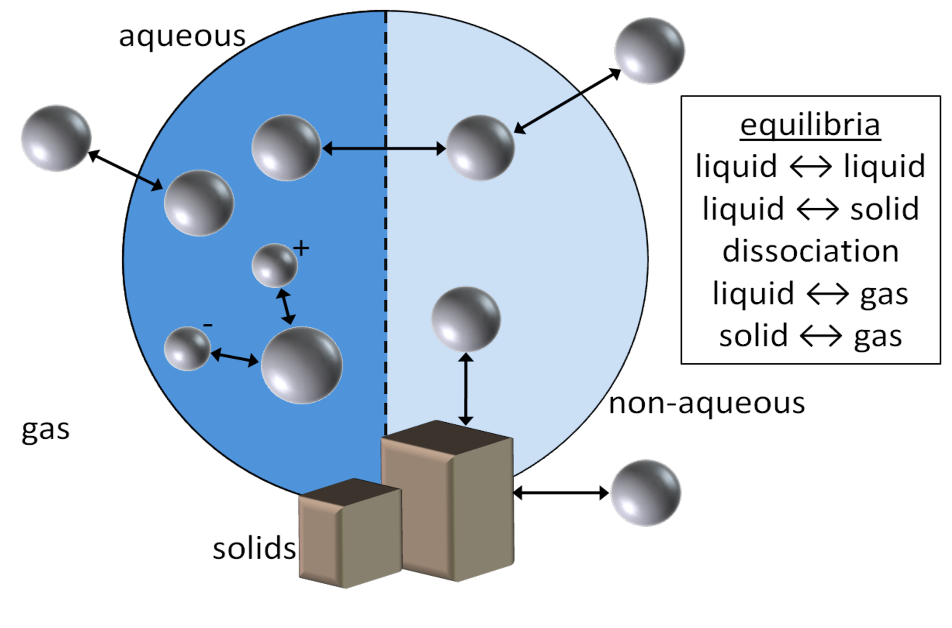
Thermodynamic Modeling of Atmospheric Aerosols: Predicting Water Content and Solute Activities

Cari S. Dutcher,*[,1] Xinlei Ge,[1] Anthony S. Wexler,[1] Simon L. Clegg[1,2]

1. Overview

Significance: Accurate predictions of atmospheric aerosol thermodynamics are central to predictions of aerosol size, optical properties, and cloud formation. However, atmospheric aerosols exhibit highly complex behavior *(right)* and lack a comprehensive thermodynamic model, especially at low relative humidities (*RH*).

Objective: Our aim is to derive an analytic thermodynamic model for electrolyte containing mixtures over the entire *RH* range.



A mixed-phase atmospheric aerosol

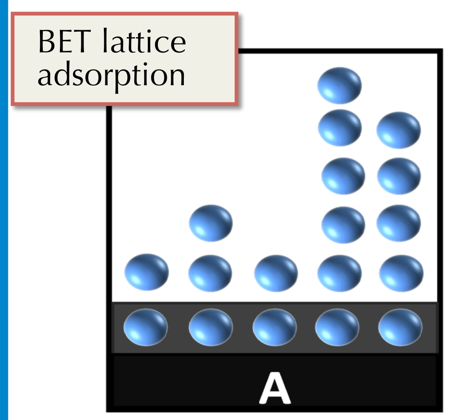
Methods: We use *statistical mechanics*, *adsorption isotherms* and *electrostatic relationships* to capture the thermodynamics of electrolyte containing solutions over the entire concentration range (detailed below). We take the unusual approach of starting with a model that is accurate at the low *RH* limit and working up to high *RH* limit. This ensures meaningful predictions when applied at low *RH*, where data is often scarce.

Support:
- National Science Foundation – Atmospheric and Geospace Sciences Postdoctoral Research Fellowship
- National Oceanic and Atmospheric Administration (grant NA07OAR4310191)
- Natural Environment Research Council (grant NE/E002641/1)
- Department of Energy (grant DE-FG02-08ER64530)

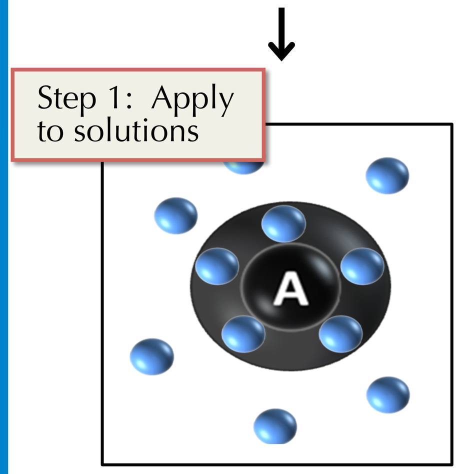
Resultant Publications:
- C.S. Dutcher, X. Ge, A.S. Wexler & S.L. Clegg. (Submitted)
- C.S. Dutcher, X. Ge, A.S. Wexler & S.L. Clegg. J Phys Chem C **116**, 1850 (2012)
- C.S. Dutcher, X. Ge, A.S. Wexler & S.L. Clegg. J Phys Chem C **115**, 16474 (2011)

Affiliations:
*Email: csdutcher@ucdavis.edu
[1]Air Quality Research Center, University of California, Davis, CA95616, USA
[2]School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK

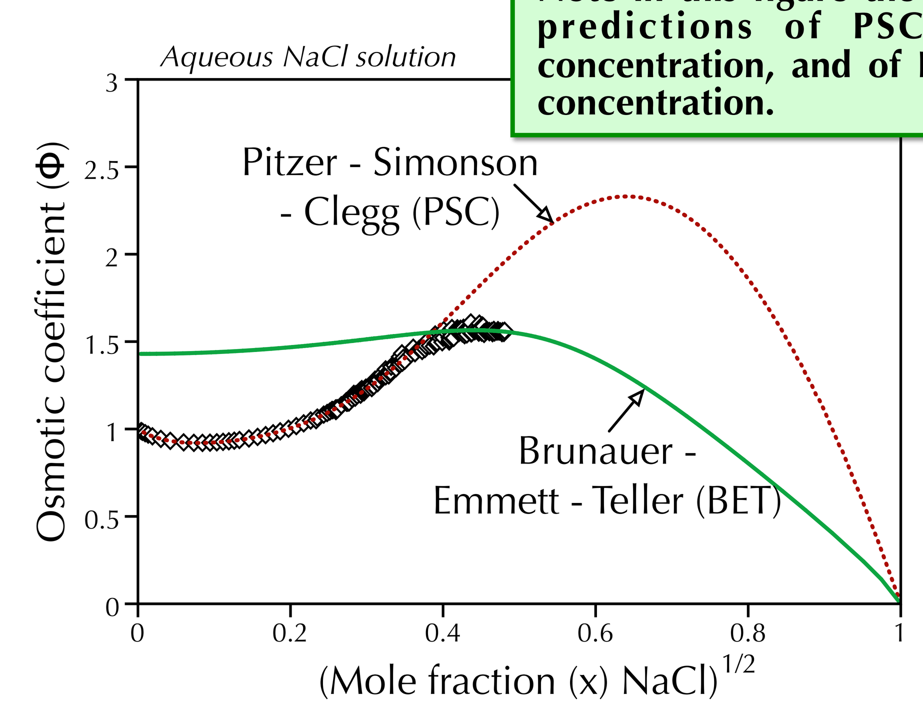
2. Model Development (Single Solute)



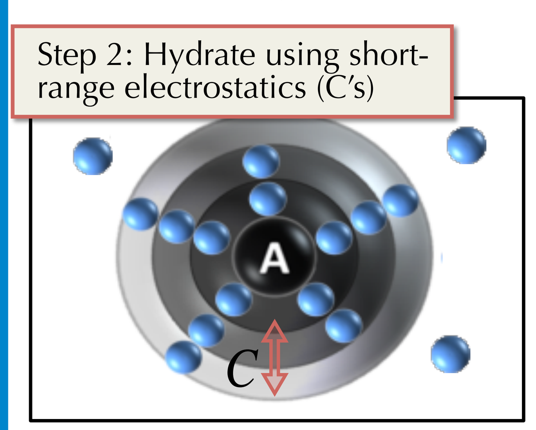
Step 1: First, we apply the statistical mechanics of Brunauer-Emmett-Teller's (BET) *lattice gas adsorption on a solid substrate* to a salt (A) in aqueous solution. Note in schematics: blue dots are water molecules.



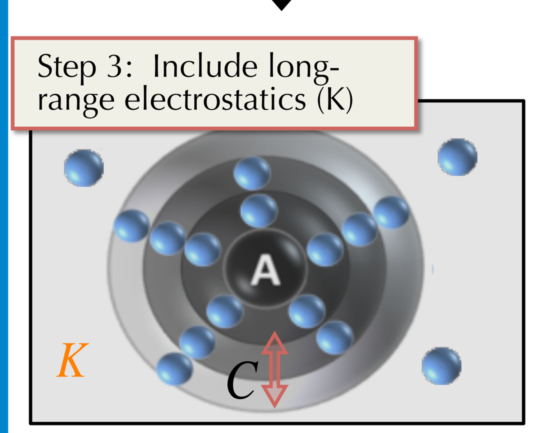
Note in this figure the inaccurate predictions of PSC at high concentration, and of BET at low concentration.



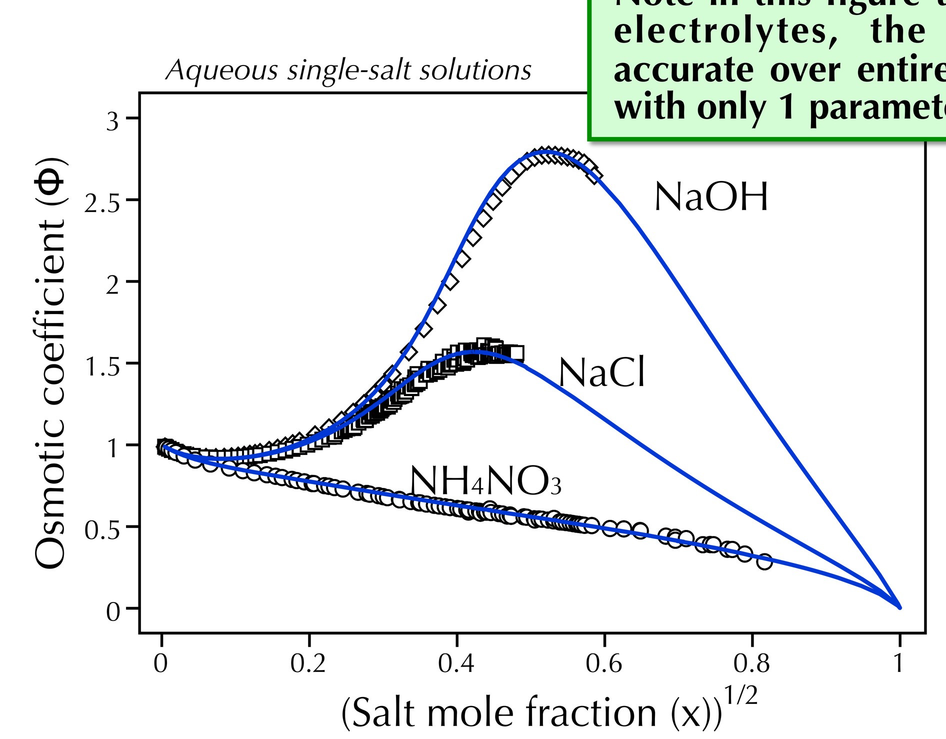
Step 2: Next, we improve the above model by accounting for the energetic costs of the *hydration of salts in water*.



Step 3: Finally, we expand the model to the *RH* = 100% limit by incorporating *electrostatic limiting law behavior (Debye-Hückel)*, similar to the long range terms seen in the PSC model.

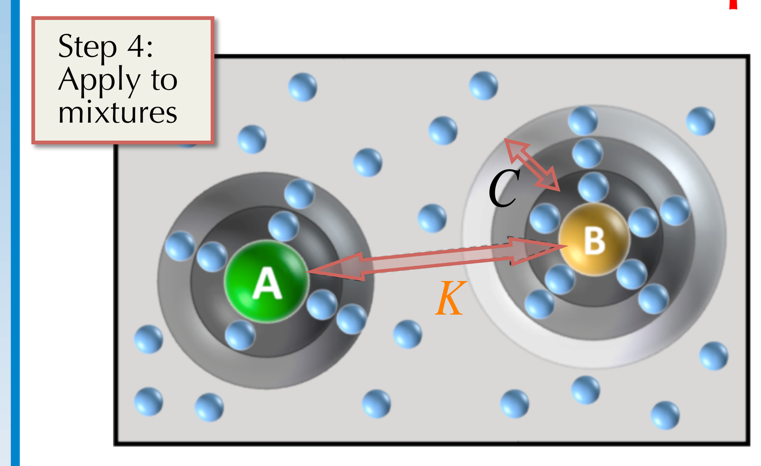


Note in this figure that for 1:1 electrolytes, the model is accurate over entire *RH* range with only 1 parameter



Single solute data (denoted with symbols): NaCl- Archer *JPCRD* 1992, Tang et al. *JPC* 1987, Cohen et al. *JPC* 1987, Chan et al. *AST* 1997. NH_4NO_3- Chan et al. *AST* 1997, Kirgintsev & Lukyanov JPC 1965, NaOH- Hamer & Wu *JPCRD* 1972.

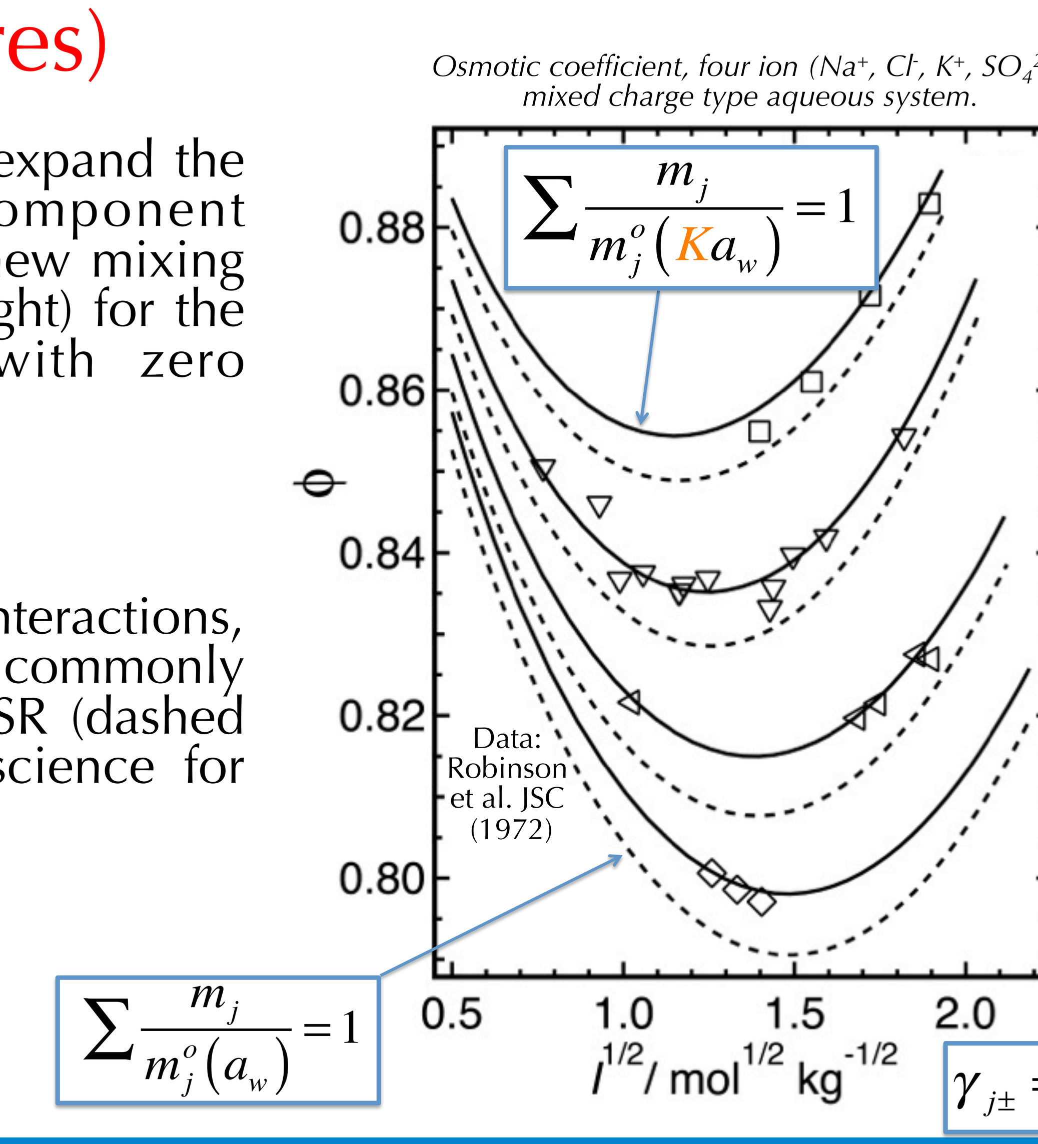
3. Model Development (Mixtures)

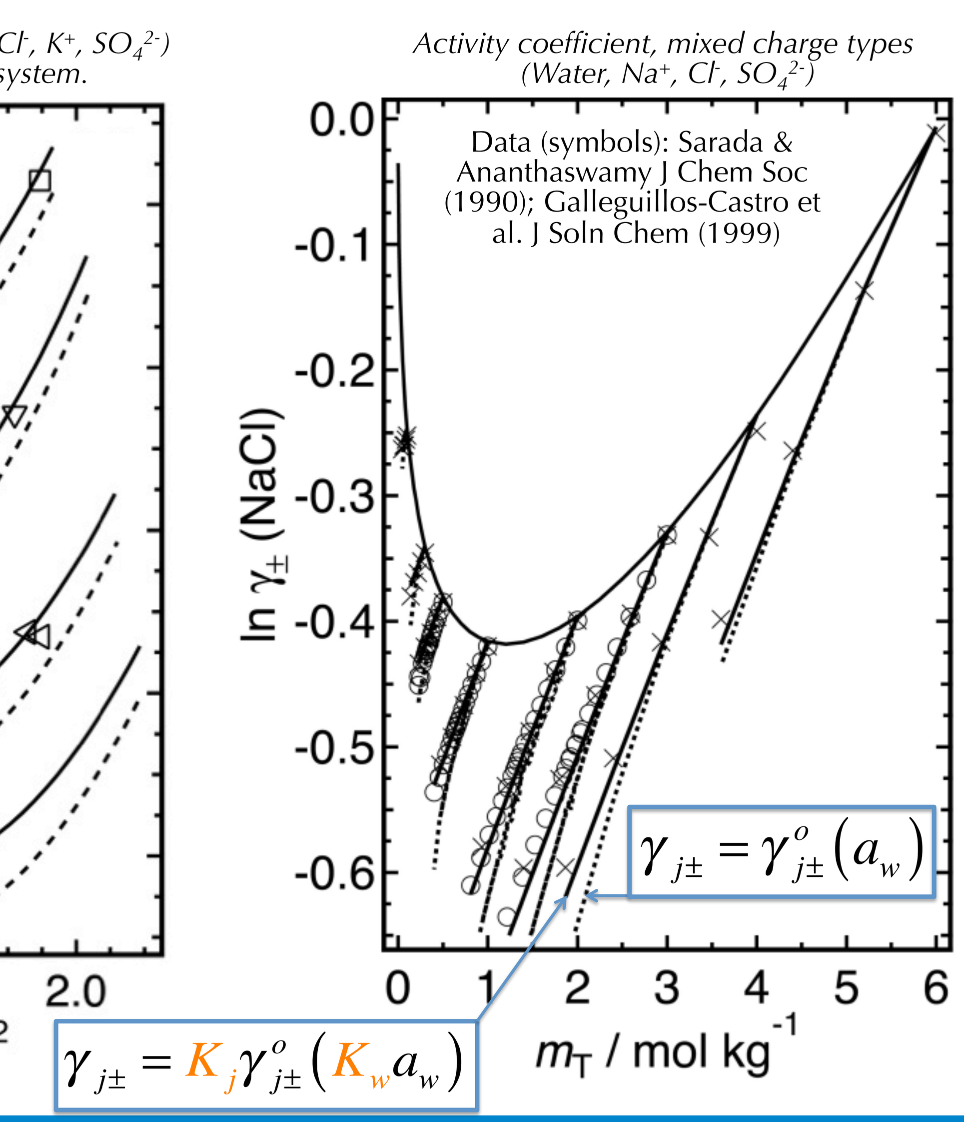


Step 4: Finally, we expand the model to multi-component systems, and find a new mixing model (solid lines, right) for the entire *RH* range with zero mixture parameters.

In the absence of solute-solute Debye-Hückel interactions, the model applied to multiple solutes yields the commonly used *Zdanovskii-Stokes-Robinson (ZSR) model*. ZSR (dashed lines, right) is commonly used in atmospheric science for estimating water contents of aerosols.

Note in the figures to the right that the mixing model with the long-range electrostatics, *K* (solid lines) improves predictions over ZSR (dashed lines) with *zero* mixture parameters.





Relating single solute concentration and water activity (3 layers):

$$m_j^o = \left(\frac{1-K_w a_w}{M_w \nu_j C_{j,1} K_w a_w}\right)\frac{\left(1-K_w a_w(1-C_{j,1})-K_w^2 a_w^2 C_{j,1}(1-C_{j,2})\right)}{\left(1-K_w a_w+K_w a_w C_{j,2}\right)\left(1-K_w a_w\right)+K_w a_w C_{j,2}}$$

Relating single solute activity and water activity (3 layers):

$$K_j a_j = \left(\frac{1-K_w a_w}{1-K_w a_w(1-C_{j,1})-K_w^2 a_w^2 C_{A,1}(1-C_{j,2})}\right)^{\nu_j}$$

Definitions

- a Activities: a_w and a_j are the water and solute j activities, respectively. Water activity is equivalent to the fractional relative humidity.
- K Long-range Debye-Hückel electrostatic expressions: K_w and K_j are calculated from known parameters (e.g. ionic strength)
- m_j Molality of solute j *(superscript 'o' denotes binary quantity)*
- $\gamma_{j\pm}$ Activity coefficient of solute j *(superscript 'o' denotes binary quantity)*
- ν_j Stoichiometric coefficient of solute j
- M_w Molecular weight of water
- $C_{j,i}$ Energy parameters for sorption to the monolayers. If intermolecular bond lengths are known, $C_{j,i}$ are calculated from Coulomb's law. If not, they are fitted to data.

4. Key Results

- Statistical mechanics, adsorption isotherms, a Debye-Hückel expression, and near-ion electrostatics combine to yield a thermodynamic model of aqueous solutions for atmospheric applications.
- *Our model predicts water and solute activities over the entire RH range* more accurately and with fewer parameters than PSC or BET models.
- The mixing model contains contains zero mixture parameter and is more accurate the ZSR model. In the limit of zero solute-solute interactions, our model reduces to the ZSR model.
- Future improvements to our model may include ion association, organic components and temperature dependence.