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Office of Environmental Management

*Hanford Field Office*

# Modernizing Soil Solution Thermodynamics by Returning to 19<sup>th</sup> Century Concepts

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# Thermodynamic Non-Ideality

- Most of us were taught in school that aqueous solution (soil solution) is never thermodynamically ideal. An ideal solution in a thermodynamic sense means that the reactivity (called the activity,  $a$ ) is equal to the concentration in mole fraction ( $x$ ) for constituent 'i'. Hence, we were taught that this equation (called Raoult's Law) is not true for electrolyte solutions like soil solution.

$$a_i = x_i$$

- Note that Raoult's Law is simplest when defined in mole fraction units. It is much more complicated when converted to molality units (moles per Kg of water) or molarity units (moles per L). Your textbook in school probably used the more complicated units, which may be why you thought thermodynamics was hard.



# Late Nineteenth Century Ideas on Ideality

- It frustrated scientists in the late 19<sup>th</sup> and early 20<sup>th</sup> centuries that aqueous solutions did not appear to follow fundamental laws like Raoult's Law.
- They believed that the apparent non-ideality occurred because the ions in solutions were not simply free ions. They either formed neutral ion-pairs, e.g.
  - $Na_{(aq)}^+ + F_{(aq)}^- \leftrightarrow NaF_{(aq)}$
- Or the ions bound some fraction of water molecules so strongly that they acted as part of the ions rather than part of the solvent, e.g.
  - $Na_{(aq)}^+ + 3H_2O \leftrightarrow Na(H_2O)_3$



# Electrostatics

- In the early 20<sup>th</sup> century, Millner, Noyes, Debye and Huckel showed that non-ideality in dilute electrolyte solutions could be explained by electrostatic interactions.
- After this discovery, most electrolyte solution thermodynamic studies either sought more and more complicated electrostatic equations to explain increasingly concentrated solutions (most common) or combined electrostatic calculations with the ion-pairing or hydration concepts (less common).



# Hydration and Ion-Pairing Today

- While thermodynamic specialists honed electrostatic models, experimentalists delved into hydration reactions and ion-pairing.
- After thousands of studies using dozens of techniques, it is now irrefutable that ions form ion-pairs and bind water strongly. See the following review articles, for instance:
  - Marcus, Y. (2010). Effect of ions on the structure of water. *Pure and Applied Chemistry*, 82(10), 1889-1899.
  - Marcus, Y., & Hefter, G. (2006). Ion pairing. *Chemical Reviews*, 106(11), 4585-4621.
- Many studies covered in those same reviews showed that the ion-pairing and hydration reactions were caused by electrostatic interactions.
- In my opinion, this means that the electrostatic, hydration, and ion-pairing concepts are not mutually exclusive, they are different sides of the same coin.



# Thermodynamics in Modern Transport Codes

- In today's computational landscape, fate and transport codes usually either omit thermodynamics and rely on simplistic assumptions for chemistry, or they use models based on electrostatic interactions. For huge system models, the electrostatic-based models are simply computationally unfeasible.
- The most common thermodynamic models used in codes are the “Pitzer” equation, developed in 1973-1974.
- Or the “SIT” model, originally developed in the 1930s, but extended to more complicated systems in the 1970s.
- Massive advancements in electrostatic models have occurred since the 1970s, but no one uses the advanced models for practical applications.
  - The Pitzer and SIT models are already computationally cumbersome.
  - The newer electrostatic models are even more complex than the Pitzer model. and thus not widely adopted for practical applications



# Zavitsas' Model

- In order to develop a more computationally reasonable model, Zavitsas jettisoned the electrostatic terms and created a model based on ion-pairing and hydration reactions alone:

$$a_w = \frac{55.509 - mH_d}{55.509 - mH_d + mi_e}$$

- He calculated the activity of water ( $a_w$ ), based on the hydration number for the electrolyte ( $H_d$ ) and the number of particles (ions or ion-pairs) that the electrolyte breaks into in a Kg of water ( $i_e$ ).





# Multicomponent Form of Zavitsas' Model

- I saw Zavitsas' model as a computationally efficient model that could be deployed in transport codes, so I derived a multicomponent form needed for real systems (see Reynolds, *AIChE J.* 68, 2022, article number e17487).

$$a_w = \frac{55.509 - \left( \sum_{j=1}^q m_j H_{(j)} \right)}{55.509 - \left( \sum_{j=1}^q m_j H_{(j)} \right) + \left( \sum_{j=1}^q m_j i_{(j)} \right)}$$

- I applied the Gibbs-Duhem condition to derive an equation for the activity of ions (see Reynolds et al., *J. Molecular Liq.* 347, 2022, article number 118309).

$$\chi_j = \frac{\sum_{j=1}^q m_j (i_j - 1)}{55.509 - \left( \sum_{j=1}^q m_j H_{(j)} \right) + \left( \sum_{j=1}^q m_j i_{(j)} \right)}$$



# Sodium Fluoride (NaF)

- NaF is a major constituent in the Hanford waste tanks with some leaking into soil.
- NaF is sparingly soluble, which means that there is a limited composition range in water.
  - The small composition range caused collinearity in the measured activity versus concentration model.
  - This means that there is more than one pair of  $H_d$  and  $i_e$  parameters that can fit the activity data just as well, and we cannot tell from statistics which is the most correct.
- For solutions with just sodium and fluoride, the collinearity is not detrimental, but it is problematic for multicomponent solutions.
- Can a different way to estimate these coefficients be found?



# Estimating the $H_d$ parameter for NaF without fitting to activity data

- The  $H_d$  parameter in Zavitsas' model is the number of water molecules that are bound to the electrolyte so strongly that they act like part of the electrolyte instead of part of the bulk water.
- Dielectric Relaxation Spectroscopy (DRS) determines the number of water molecules bound to ions so strongly that they rotate along with the ions as they diffuse in water.
- The number of water molecules strongly bound to NaF has been determined previously to be 4.9 by DRS (Buchner et al., *J. Phys. Chem.* 123, 2019, pg. 10,868.)
- I assumed that the strongly bound water molecules determined by DRS are the same as  $H_d$  in Zavitsas' model (4.9).



# Is there a way to estimate the $i_e$ parameter?

- Collins' Law of Matching Water Affinities (Collins, *Biophysical journal*, 72(1), 1997, 65-76) assumes that the extent of ion-pairing is proportional to how strongly the ions bind water.
  - When the cation and anion bind water similarly to each other, they are more likely to form an ion-pair than stay as free ions.
- But how to quantify how strongly the ions bind water?
- There is an empirical model of solution viscosity (viscosity versus concentration) called the "Jones-Dole" model.
- Collins and others have argued that the empirical B parameter in the Jones-Dole model (called the "Viscosity B" parameter) is proportional to the strength that ions bind water.
- The viscosity B parameter has been tabulated in the literature for many ions.

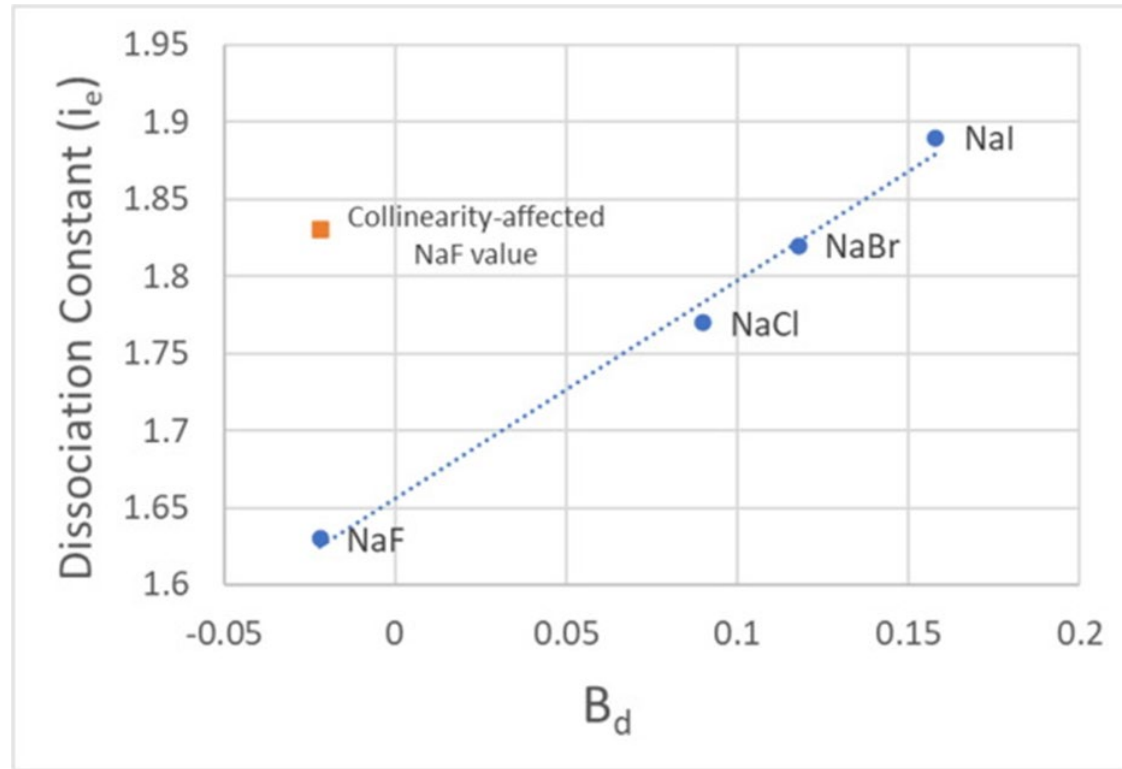


# Estimating the $i_e$ parameter

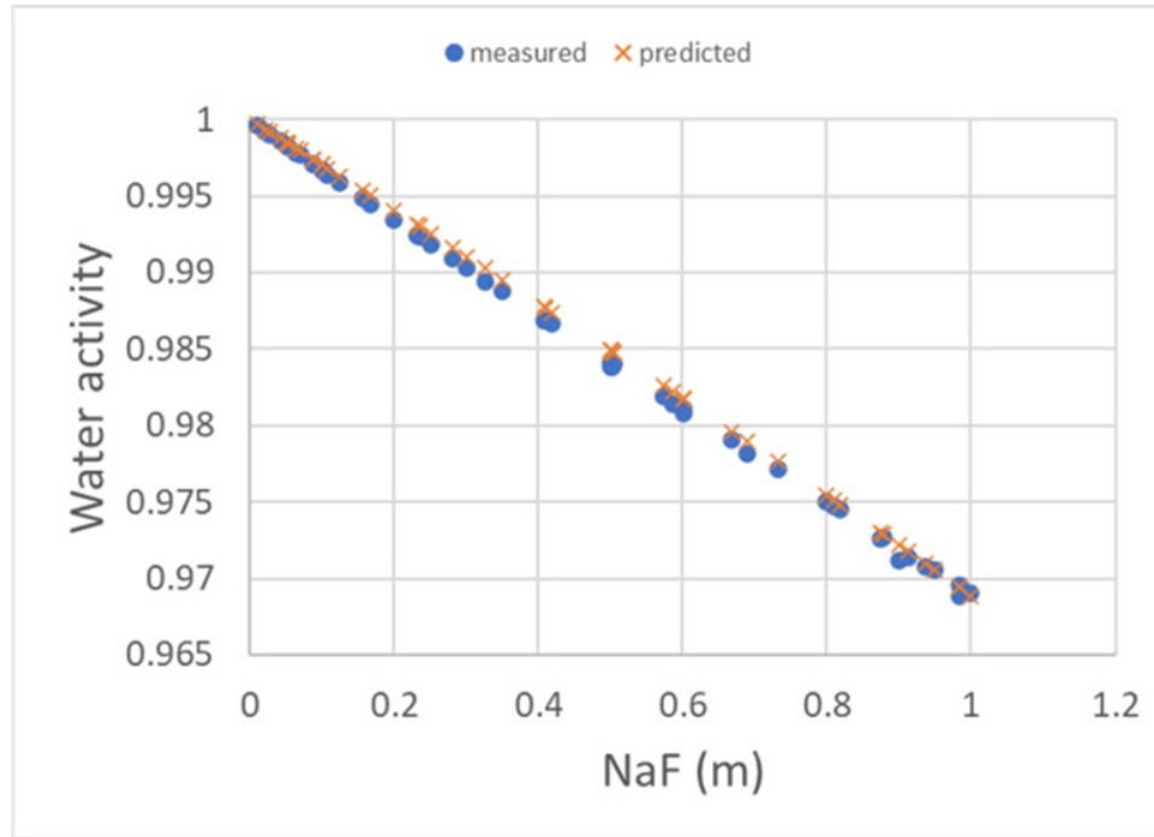
- Zavitsas has shown that the  $i_e$  parameter for electrolytes is proportional to the difference between the Viscosity B for cation and anion ( $B_d$ ).
- I plotted the difference between the Viscosity B parameters for sodium and three halides (chloride, bromide, and iodide) and correlated them to the  $i_e$  parameters published by Zavitsas, developing a regression equation for sodium-halides.
- $i_e = 1.645 + 1.502(B_d)$
- This equation was used to estimate  $i_e$  for NaF.



# The $i_e$ parameters versus $B_d$ For sodium-halides



# How good are these estimates?

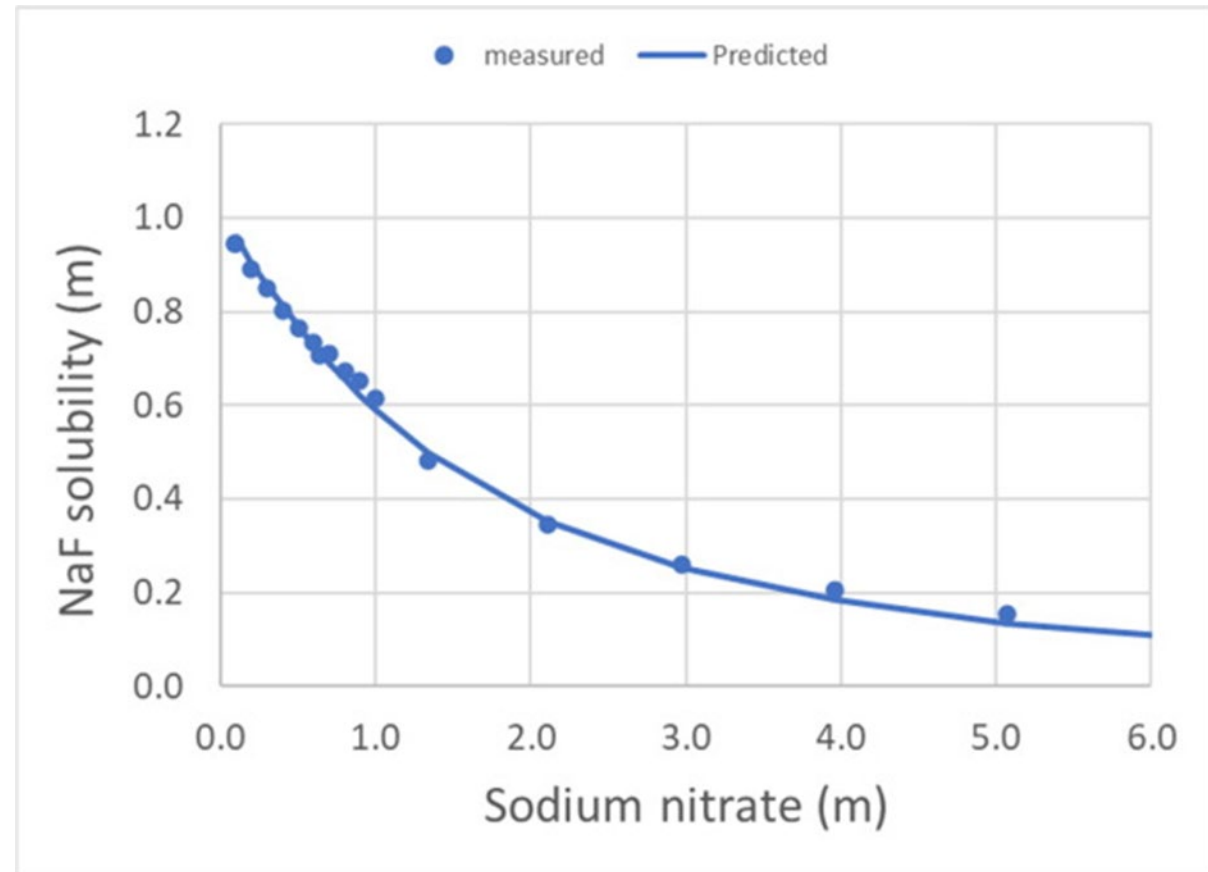


- The estimated  $H_d$  and  $i_e$  parameters were used to calculate the activity of water in NaF solutions and compared to experimental data. There is only a small bias. All values are within 0.1% of experimental values.



# How well can solubility be predicted?

- The parameters were used to calculate NaF solubilities in mixtures with sodium nitrate, where experimental data was readily available and relevant to Hanford.
- The fit was excellent, even though no parameters were determined by fitting the model to solubility data.
- In contrast, the Pitzer model had to be force-fit to this solubility data with five fitted parameters.





# Conclusions

- Zavitsas' Model was expanded to multicomponent solutions
- If DRS data and Viscosity B coefficients are available (the latter being available for almost any ion you can think of), model parameters can be estimated, even for electrolytes that are not very soluble.
- The solubility of NaF in complex multicomponent solutions could be predicted accurately without fitting the model to thermodynamic or solubility data. I know of no other model where that would be true.
- Zavitsas' model is computationally efficient (can be easily solved with hand calculator) and can be deployed in complex fate and transport codes.



# Backup Slide: Is Zavitsas' model ready for prime time?

- I have tested the model for dozens of monovalent electrolytes in multicomponent mixtures, with excellent results for the overwhelming majority of them.
- An evaluation of systems containing divalent cations is still required.
- The few systems that the model has predicted poorly all contain divalent oxyanions (carbonate, sulfate, and chromate), which are unfortunately important to Hanford.
  - A clever person could likely find a modification that would accommodate these oxyanions. I am still looking for an epiphany.
  - If all else fails, the Pitzer model could be used for divalent oxyanions and Zavitsas' model for everything else.
- A method to parametrize the model for extremely low solubility electrolytes (like uranium) would need to be developed, but this seems doable.

