

Statistical Mechanics of Multilayer Sorption: Surface Tension

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1. Overview

Significance: Surface tension governs nucleation, nuclei growth to CCN, and activation, yet current models of surface tension as a function of concentration cannot handle both organics and electrolytes in water.

Objective: Derive fundamental expressions for surface tension as a function of concentration that are accurate over the full RH range and for arbitrary solute characteristics.

Methods: We use *statistical mechanical adsorption isotherms* to model the replacement of solvent (water) molecules at the solution surface by solutes (electrolytes, organics) adsorbing onto the surface. The methods are based on the same statistical mechanics used by Dutcher and coworkers (2011, 2012, 2013), except that the solute may displace an arbitrary, and on average non-integer, number of solvent molecules from the surface.

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Resultant Publications:

- CS Dutcher, X Ge, AS Wexler & SL Clegg. (in press), (2013)
- CS Dutcher, X Ge, AS Wexler & SL Clegg. J Phys Chem C **116**, 1850 (2012)
- CS Dutcher, X Ge, AS Wexler & SL Clegg. J Phys Chem C **115**, 16474 (2011)
- CS Dutcher, AS Wexler & SL Clegg. J Phys Chem C **114**, 12216 (2010)

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2. Model Development

Surface Displacement Partition Function:

$$\Omega_1 = \frac{N_{WS}!(r_A)}{(N_{WS} - r_A N_{A1})!(r_A) (r_A N_{A1})!(r_A)}$$

Assumes that the surface is fluid

Assumes that solute A pushes r_A waters off the surface

Surface-Bulk Interactions Partition Function:

$$\Omega_2 = \frac{N_A!}{N_{A1}!(N_A - N_{A1})!}$$

Assumes all multilayer solute has same energy

Energy of Surface Water, Adsorbed Solute and Bulk Solute:

$$E = -N_{WS}\epsilon_{WS} - N_{A1}\epsilon_{A1} - N_A\epsilon_A$$

ϵ_{A1} = energy of A in layer 1

ϵ_A = energy of A in multilayer

ϵ_{WS} = energy of water at the surface

Gibbs Free Energy is

$$\frac{G}{kT} = \frac{E}{kT} - \ln \Omega_1 \Omega_2$$

Minimize Gibbs energy to get surface/bulk partitioning of A

$$\frac{\partial G/kT}{\partial N_{A1}} = \frac{1}{kT} \frac{\partial E}{\partial N_{A1}} - \frac{\partial \ln \Omega}{\partial N_{A1}} = 0$$

Derivative of G/kT with respect to N_A gives solute activity:

$$K_A a_A = 1 - N_{A1}/N_A$$

2. Model Development (Continued)

Derivative of G/kT with respect to A gives Surface Tension:

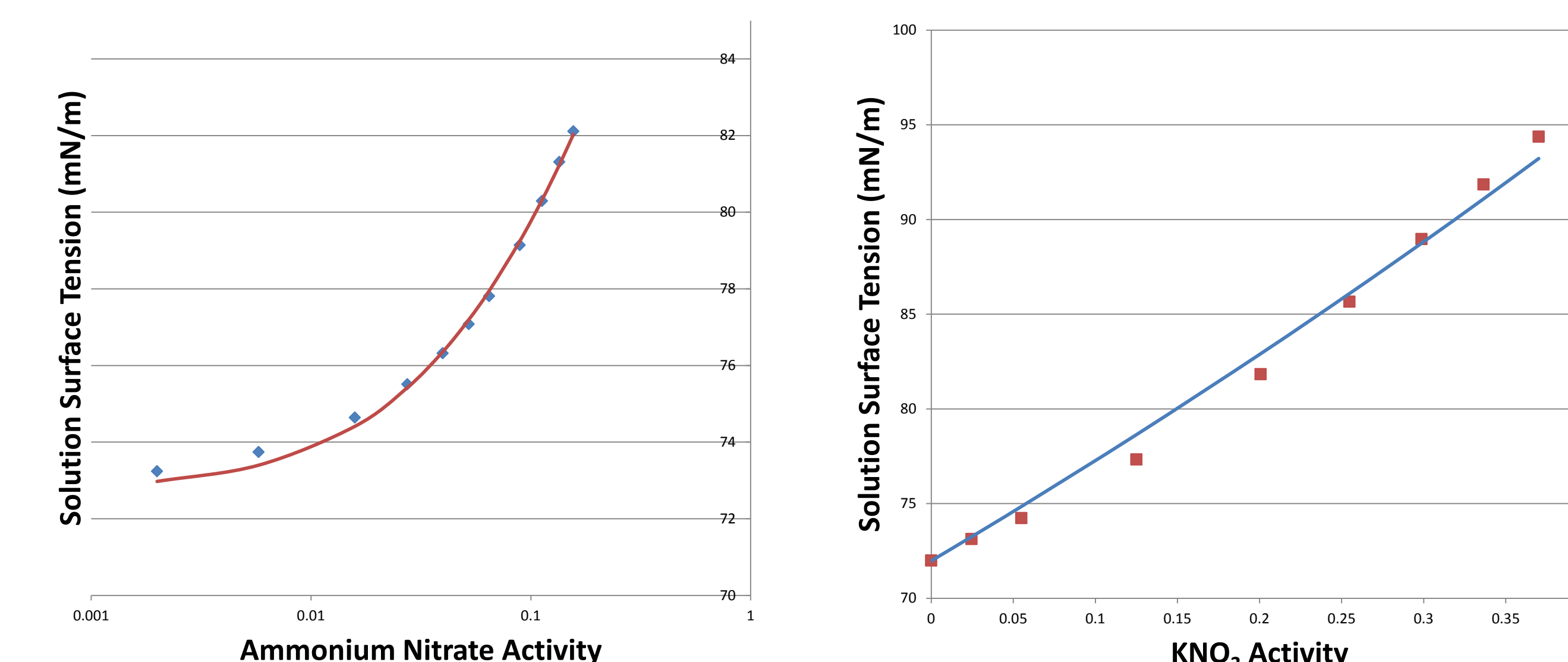
$$\sigma = \frac{\partial G}{\partial A_T} = \frac{kT}{S_W} \frac{\partial(G/kT)}{\partial N_{WS}} = \frac{kT}{r_A S_W} \ln \left(1 - \frac{r_A N_{A1}}{N_{WS}} \right)$$

giving

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

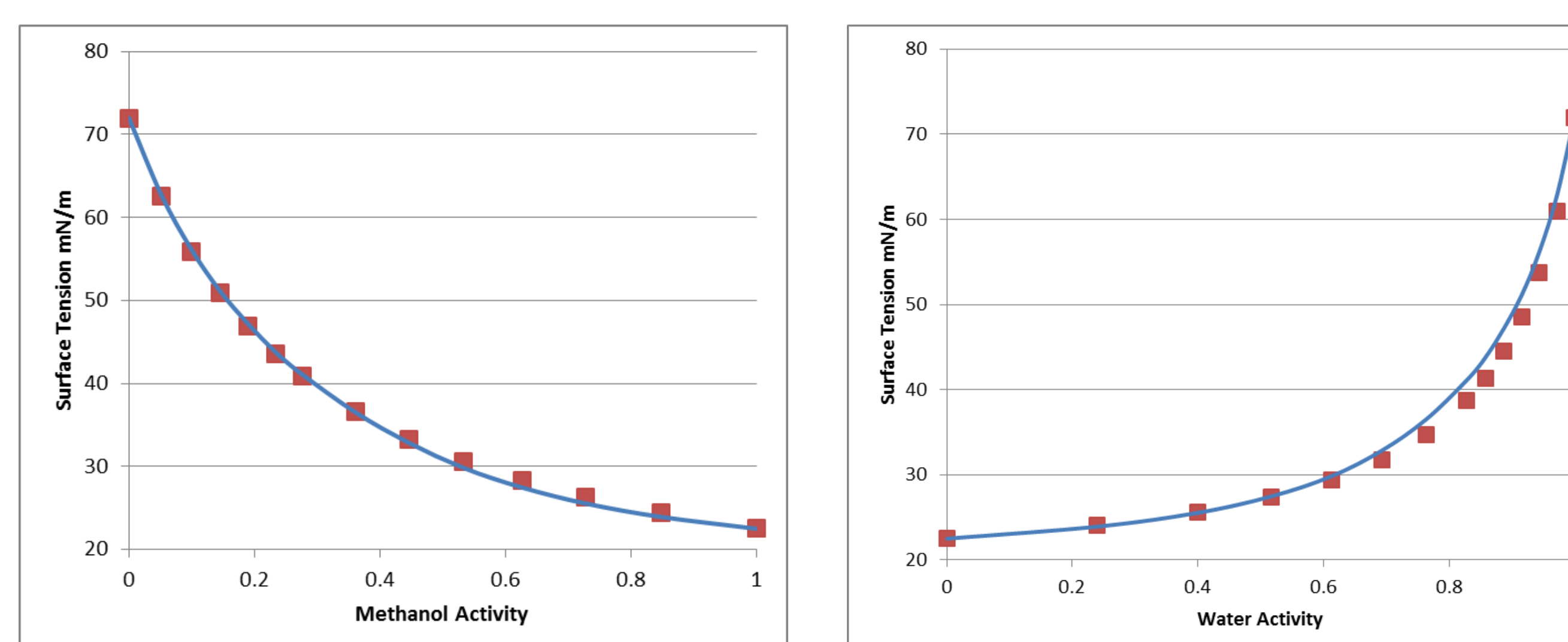
3. Examples (electrolytes)

Ammonium Nitrate and Potassium Nitrate

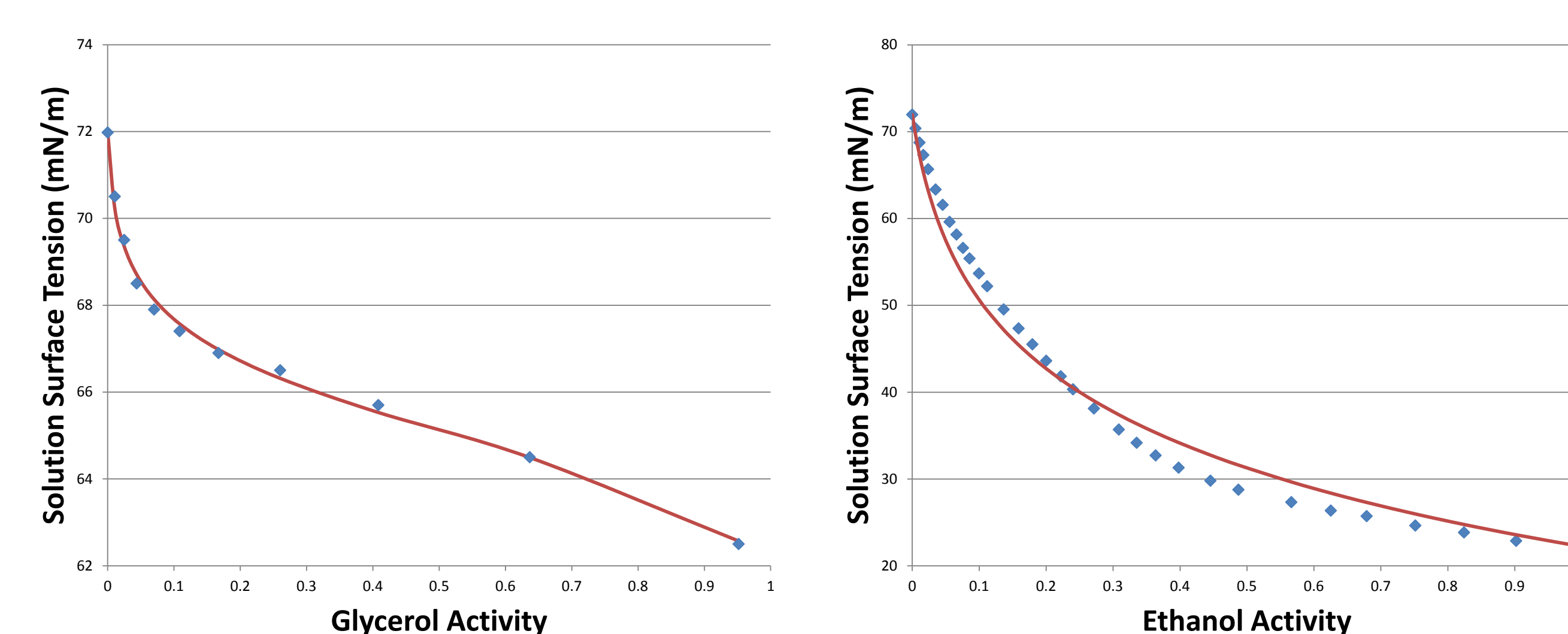


3. Examples (organic)

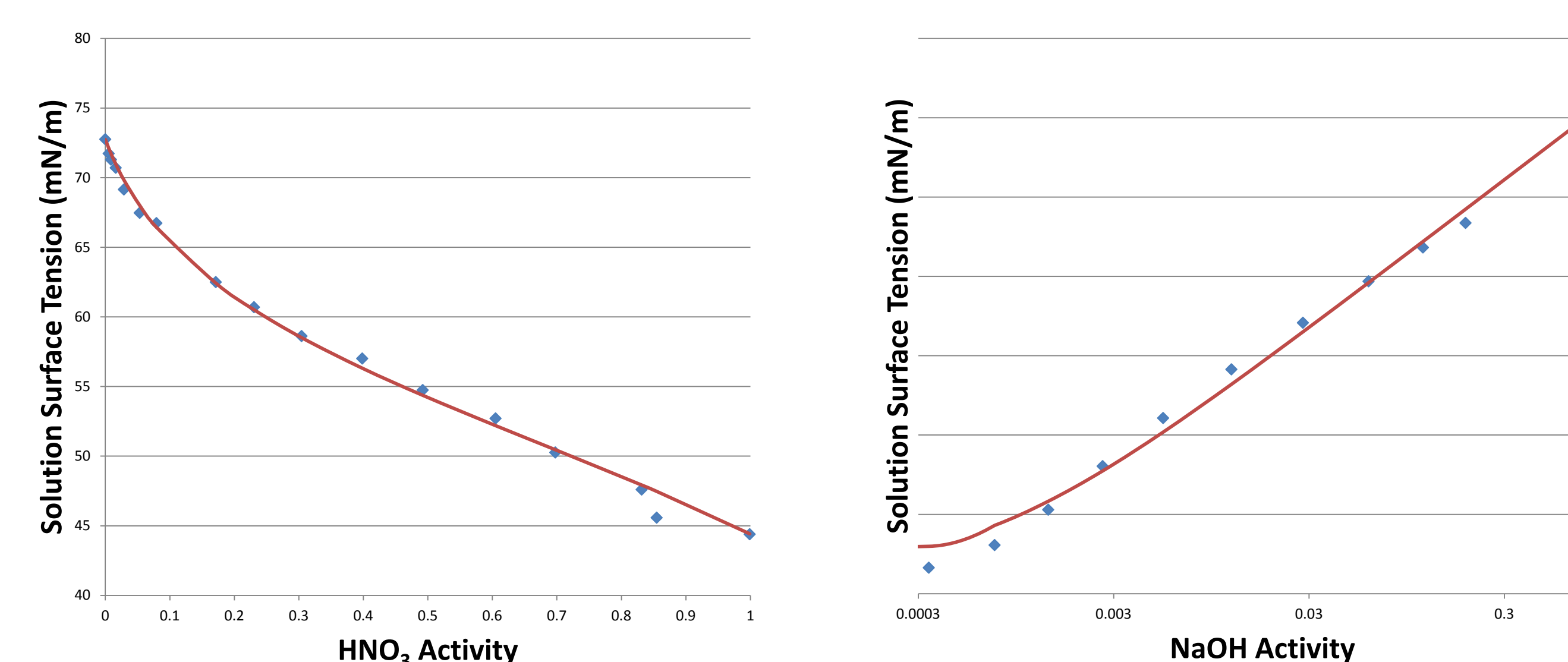
Methanol in Water / Water in methanol



Glycerol in Water and Ethanol in water



Nitric Acid and Sodium Hydroxide



4. Key Results

- New equation for surface tension vs. concentration
- Works equally well for electrolytes and organics
- Only 1-3 fit parameters per solute
- Accurate over the full concentration range
- Same formalism as GAB; incorporates solute and solvent size
- Pure electrolyte surface tension predictions agrees with prior work (Dutcher et al., 2010)