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Supporting Information for "A Statistical Thermodynamic Model for Surface Tension of Organic and Inorganic Aqueous Mixtures"

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Statistical Mechanical Derivation for an Arbitrary Number of Solutes

For an arbitrary number of solutes, *n*, we define the number of possible configurations of at the surface in eq S1, the surface partition function. Subscript *j* of the first multiplicative sum represents the solute that adsorbs at the surface (or bulk) first, where each solute in the system from A to Z has this position (*n*-1)! times. Solute *k* of the next multiplicative sum represents all solutes except for *j*, with the notation $k < j$ meaning the subsequent solutes that have the second spot in line (*n*-2)! times. The multiplicative sums are defined as needed for however many solutes are in the system. With this approach, there is a unique combination for each permutation of solute adsorption, making a total of *n*! possible surface partition functions. Therefore, the entire product is raised to the power 1/*n*!, resulting in

$$\Omega_{surface} = \left\{ \prod_{j}^{Z} \prod_{k<j} \prod_{l<k} \cdots \frac{N_{WS}!_{r_j}^{(n-1)!} \left(N_{WS} - r_k N_{kS}\right)!_{r_j}^{(n-2)!} \left(N_{WS} - r_k N_{kS} - r_l N_{lS}\right)!_{r_j}^{(n-3)!} \cdots}{\left(r_j N_{jS}\right)!_{r_j}^{n!} \left(N_{WS} - r_j N_{jS}\right)!_{r_j}^{(n-1)!} \left(N_{WS} - r_j N_{jS} - r_k N_{kS}\right)!_{r_k}^{(n-2)!} \left(N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}\right)!_{r_l}^{(n-3)!} \cdots} \right\}^{1/n!} \quad \text{(S1)}$$

The bulk partition function represents mixing between the surface and the bulk for each solute:

$$\Omega_{bulk} = \prod_{j=A}^{Z} \frac{N_j!}{N_{jS}!\,(N_j - N_{jS})!} \tag{S2}$$

Gibbs free energy, $G \approx E - TS$, must be found next. We obtain an expression for entropy through Boltzmann's equation, $S = k_B Ln\Omega_{bulk}\Omega_{surface}$, giving

$$\begin{aligned}
\frac{S}{k_B} &= \frac{1}{n!}\Bigg\{\sum_{j=A}^{Z} N_j Ln\left(\frac{N_j}{N_j - N_{jS}}\right) \\
&+ \sum_{k<j}\sum_{l<k}\cdots\frac{N_{WS}}{r_j} Ln\left(\left(\frac{N_{WS}}{N_{WS} - r_j N_{jS}}\right)^{(n-1)!}\left(\frac{r_k(N_{WS} - r_k N_{kS})}{r_j(N_{WS} - r_j N_{jS} - r_k N_{kS})}\right)^{(n-2)!}\left(\frac{r_l(N_{WS} - r_k N_{kS} - r_l N_{lS})}{r_j(N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS})}\right)^{(n-3)!}\cdots\right) \\
&+ N_{jS} Ln\left(\left(\frac{N_j - N_{jS}}{{N_{jS}}^2}\right)^{n!}\left(\frac{N_{WS} - r_j N_{jS}}{r_j}\right)^{(n-1)!}\left(\frac{N_{WS} - r_j N_{jS} - r_k N_{kS}}{r_k}\right)^{(n-2)!r_j/r_k}\left(\frac{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}}{r_l}\right)^{(n-3)!r_j/r_l}\cdots\right) \\
&+ N_{kS} Ln\left(\left(\frac{N_{WS} - r_j N_{jS} - r_k N_{kS}}{r_k}\right)^{(n-2)!}\left(\frac{r_j}{(N_{WS} - r_k N_{kS})}\right)^{(n-2)!r_k/r_j}\left(\frac{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}}{r_l}\right)^{(n-3)!r_k/r_l}\left(\frac{r_j}{N_{WS} - r_k N_{kS} - r_l N_{lS}}\right)^{(n-3)!r_k/r_j}\cdots\right) \\
&+ N_{lS} Ln\left(\left(\frac{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}}{r_l}\right)^{(n-3)!}\left(\frac{r_j}{N_{WS} - r_k N_{kS} - r_l N_{lS}}\right)^{(n-3)!r_l/r_j}\cdots\right)\cdots\Bigg\}.
\end{aligned} \tag{S3}$$

The total energy is the sum of molecular energies of waters at the surface (ε_{WS}), waters in the bulk (ε_{WB}), solutes at the surface (ε_{jS}) and solutes in the bulk (ε_{jB}) multiplied by the number of each, giving

$$E = -N_{WS}\Delta\varepsilon_{WS} - N_W\varepsilon_{WB} - \sum_{j=A}^{Z}\left(N_{jS}\Delta\varepsilon_{jS} - N_j\varepsilon_{jB}\right) \tag{S4}$$

Solute activity is the derivative of G with respect to number of solutes in the system, N_j, resulting in

$$K_j a_j = 1 - \frac{N_{jS}}{N_j} \tag{S5}$$

where $K_j = exp\left(\frac{\Delta\varepsilon_{jB}}{k_BT}\right)$. Equilibrium partitioning of a solute between the surface and bulk is imposed by taking the derivative of G with respect to number of solutes at the surface, N_{jS}, and setting it equal to zero, resulting in

$$\begin{aligned} C_j &= exp\left(\frac{\Delta\varepsilon_{jS}}{k_BT}\right) \\ &= \prod_{k<j}\prod_{l<k}\cdots\frac{{N_{jS}}^2}{N_j - N_{jS}}\Bigg\{\left(\frac{r_j}{N_{WS} - r_jN_{jS}}\right)^{(n-1)!}\left(\frac{r_j}{N_{WS} - r_jN_{jS} - r_kN_{kS}}\right)^{(n-2)!} \\ &\quad\times\left(\frac{r_j}{N_{WS} - r_jN_{jS} - r_kN_{kS} - r_lN_{lS}}\right)^{(n-3)!} \\ &\quad\times\left(\frac{N_{WS} - r_jN_{jS}}{N_{WS} - r_jN_{jS} - r_kN_{kS}}\right)^{(n-2)!r_j/r_k} \\ &\quad\times\left(\frac{N_{WS} - r_jN_{jS} - r_kN_{kS}}{N_{WS} - r_jN_{jS} - r_kN_{kS} - r_lN_{lS}}\right)^{(n-3)!r_j/r_l} \\ &\quad\times\left(\frac{N_{WS} - r_jN_{jS} - r_kN_{kS}}{r_k}\right)^{(n-3)!r_j/r_l} \\ &\quad\times\left(\frac{r_l}{N_{WS} - r_jN_{jS} - r_kN_{kS} - r_lN_{lS}}\right)^{(n-3)!r_j/r_l}\Bigg\}^{\frac{1}{n!}} \end{aligned} \tag{S6}$$

Surface tension is obtained by taking the derivative of G with respect to area, approximated as the projected area of one water molecule, S_W, times the maximum number of waters at the surface,

N_{WS}. There are also solutes at the surface, so area occupied by solutes is actually $r_j N_{jS} S_W$ and the area occupied by waters is $S_W(N_{WS} - r_j N_{jS})$, making the total area $S_W N_{WS}$. The expression for surface tension is

$$\sigma = \sigma_w + \sum_{j=A}^{Z} \sum_{k<j} \sum_{l<k} \cdots \frac{kT}{r_j S_W} \frac{1}{n!} Ln \left(\begin{array}{c} \left(\frac{N_{WS} - r_j N_{jS}}{N_{WS}}\right)^{(n-1)!} \left(\frac{r_j\left(N_{WS} - r_j N_{jS} - r_k N_{kS}\right)}{r_k(N_{WS} - r_k N_{kS})}\right)^{(n-2)!} \\ \left(\frac{r_j\left(N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}\right)}{r_l(N_{WS} - r_k N_{kS} - r_l N_{lS})}\right)^{(n-3)!} \cdots \end{array} \right) \quad \text{(S7)}$$

Equations S3, S6, and S7 are evaluated for 1, 2, and 3 solute systems in the Supporting Information in Tables S1-S3. Let $\chi_{AB} = N_{WS} - r_A N_{AS} - r_B N_{BS}$, $\chi_{AC} = N_{WS} - r_A N_{AS} - r_C N_{CS}$, $\chi_{ABC} = N_{WS} - r_A N_{AS} - r_B N_{BS} - r_C N_{CS}$, and so forth.

Table S1: Equation 3 evaluated for solutions containing one, two, and three solutes.

Number of solutes (n)	Entropy (S/k_B)
n=1	$N_A Ln\left(\frac{N_A}{N_A - N_{AS}}\right) + \frac{N_{WS}}{r_A}\left(\frac{N_{WS}}{N_{WS} - r_A N_{AS}}\right) + \frac{(N_{WS} - r_A N_{AS})(N_A - N_{AS})}{r_A {N_{AS}}^2}$
n=2	$N_A Ln\frac{N_A}{(N_A - N_{AS})} + N_B Ln\frac{N_B}{(N_B - N_{BS})} + \frac{N_{WS}}{2r_A} Ln\frac{N_{WS}(N_{WS} - r_B N_{BS})}{\chi_{AB}(N_{WS} - r_A N_{AS})}$ $+ \frac{N_{WS}}{2r_B} Ln\frac{N_{WS}(N_{WS} - r_A N_{AS})}{\chi_{AB}(N_{WS} - r_B N_{BS})} + \frac{r_A N_{AS}}{2r_B} Ln\frac{\chi_{AB}}{(N_{WS} - r_A N_{AS})}$ $+ \frac{r_B N_{BS}}{2r_A} Ln\frac{\chi_{AB}}{(N_{WS} - r_B N_{BS})}$ $+ \frac{N_{AS}}{2} Ln\frac{\chi_{AB}(N_{WS} - r_A N_{AS})(N_A - N_{AS})^2}{{r_A}^2 {N_{AS}}^4}$ $+ \frac{N_{BS}}{2} Ln\frac{\chi_{AB}(N_{WS} - r_B N_{BS})(N_B - N_{BS})^2}{{r_B}^2 {N_{BS}}^2}$

n=3	$$N_A Ln\frac{N_A}{(N_A-N_{AS})}+N_B Ln\frac{N_B}{(N_B-N_{BS})}+N_C Ln\frac{N_C}{(N_C-N_{CS})}$$ $$+\frac{N_{AS}}{6}Ln\left[\frac{(N_A-N_{AS})^6\chi_{AB}\chi_{AC}\chi_A{}^2\chi_{ABC}{}^2}{r_A N_{AS}{}^{12}}\right]$$ $$+\frac{N_{BS}}{6}Ln\left[\frac{(N_B-N_{BS})^6\chi_{AB}\chi_{BC}\chi_B{}^2\chi_{ABC}{}^2}{r_B N_{BS}1^2}\right]$$ $$+\frac{N_{CS}}{6}Ln\left[\frac{(N_C-N_{CS})^6\chi_{AC}\chi_{BC}\chi_C{}^2\chi_{ABC}{}^2}{r_C N_{CS}{}^{12}}\right]$$ $$+\frac{N_{WS}}{6r_A}Ln\frac{N_{WS}{}^2\chi_B\chi_C\chi_{BC}{}^2}{\chi_{AC}\chi_{AB}\chi_A{}^2\chi_{ABC}{}^2}+\frac{N_{WS}}{6r_B}Ln\frac{N_{WS}{}^2\chi_A\chi_C\chi_{AC}{}^2}{\chi_{BC}\chi_{AB}\chi_B{}^2\chi_{ABC}{}^2}$$ $$+\frac{N_{WS}}{6r_C}Ln\frac{N_{WS}{}^2\chi_A\chi_B\chi_{AB}{}^2}{\chi_{AC}\chi_{BC}\chi_C{}^2\chi_{ABC}{}^2}+\frac{r_A N_{AS}}{6r_B}Ln\frac{\chi_{AB}\chi_{ABC}{}^2}{\chi_A\chi_{AC}{}^2}$$ $$+\frac{r_A N_{AS}}{6r_C}Ln\frac{\chi_{AC}\chi_{ABC}{}^2}{\chi_A\chi_{AB}{}^2}+\frac{r_B N_{BS}}{6r_C}Ln\frac{\chi_{BC}\chi_{ABC}{}^2}{\chi_B\chi_{AB}{}^2}+\frac{r_B N_{BS}}{6r_A}Ln\frac{\chi_{AB}\chi_{ABC}{}^2}{\chi_B\chi_{BC}{}^2}$$ $$+\frac{r_C N_{CS}}{6r_B}Ln\frac{\chi_{BC}\chi_{ABC}{}^2}{\chi_C\chi_{AC}{}^2}+\frac{r_C N_{CS}}{6r_A}Ln\frac{\chi_{AC}\chi_{ABC}{}^2}{\chi_C\chi_{BC}{}^2}$$

Table S2: Equation 6 evaluated for solutions containing one, two, and three solutes.

Number of solutes (n)	C_i
n=1	$C_A = \frac{r_A {N_{AS}}^2}{(N_A - N_{AS})(N_{WS} - r_A N_{AS})}$
n=2	$C_A = \frac{r_A {N_{AS}}^2}{N_A - N_{AS}} \left(\frac{\left(\frac{N_{WS} - r_A N_{AS}}{\chi_{AB}}\right)^{r_A/r_B}}{(N_{WS} - r_A N_{AS})\chi_{AB}} \right)^{1/2}$
n=3	$C_A = \frac{r_A {N_{AS}}^2}{N_A - N_{AS}} \left(\frac{\left(\frac{(N_{WS} - r_A N_{AS}){\chi_{AC}}^2}{\chi_{AB}{\chi_{ABC}}^2}\right)^{r_A/r_B} \left(\frac{(N_{WS} - r_A N_{AS}){\chi_{AB}}^2}{\chi_{AC}{\chi_{ABC}}^2}\right)^{r_A/r_C}}{\chi_{AB}\chi_{AC}(N_{WS} - r_A N_{AS})^2{\chi_{ABC}}^2} \right)^{1/6}$

Table S3: Equation 7 evaluated for solutions containing one, two, and three solutes.

Number of solutes (n)	Surface Tension (σ)
n=1	$\sigma = \sigma_w + \frac{kT}{r_A S_W} Ln\left(\frac{N_{WS} - r_A N_{AS}}{N_{WS}}\right)$
n=2	$\sigma = \sigma_w + \frac{kT}{2r_A S_w} Ln\left[\frac{\chi_{AB}(N_{WS} - r_A N_{AS})}{N_{WS}(N_{WS} - r_B N_{BS})}\right] + \frac{kT}{2r_B S_w} Ln\left[\frac{\chi_{AB}(N_{WS} - r_B N_{BS})}{N_{WS}(N_{WS} - r_A N_{AS})}\right]$
n=3	$\sigma = \sigma_w + \frac{kT}{6r_A S_w} Ln\left[\frac{\chi_{AB}\chi_{AC}{\chi_{ABC}}^2(N_{WS} - r_A N_{AS})^2}{{N_{WS}}^2{\chi_{BC}}^2(N_{WS} - r_B N_{BS})(N_{WS} - r_C N_{CS})}\right]$ $+ \frac{kT}{6r_B S_w} Ln\left[\frac{\chi_{AB}\chi_{BC}{\chi_{ABC}}^2(N_{WS} - r_B N_{BS})^2}{{N_{WS}}^2{\chi_{AC}}^2(N_{WS} - r_A N_{AS})(N_{WS} - r_C N_{CS})}\right]$ $+ \frac{kT}{6r_C S_w} Ln\left[\frac{\chi_{AC}\chi_{BC}{\chi_{ABC}}^2(N_{WS} - r_C N_{CS})^2}{{N_{WS}}^2{\chi_{AB}}^2(N_{WS} - r_A N_{AS})(N_{WS} - r_B N_{BS})}\right]$

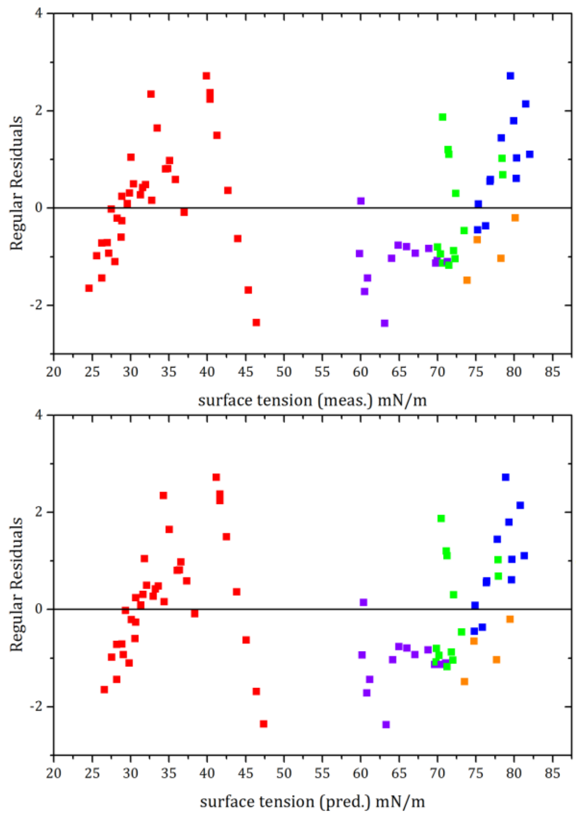

Figure S1: Residuals for surface tension (σ) model predictions and measurements for various aqueous solutions: Ethanol-glycerol (red),[1] NaCl-KCl (blue)[2], NaCl-succinic acid (green)[3], NH_4NO_3 – $(NH_4)_2SO_4$ (orange; taken by author with Wilhelmy plate), NaCl-glutaric acid (purple; optical tweezers).

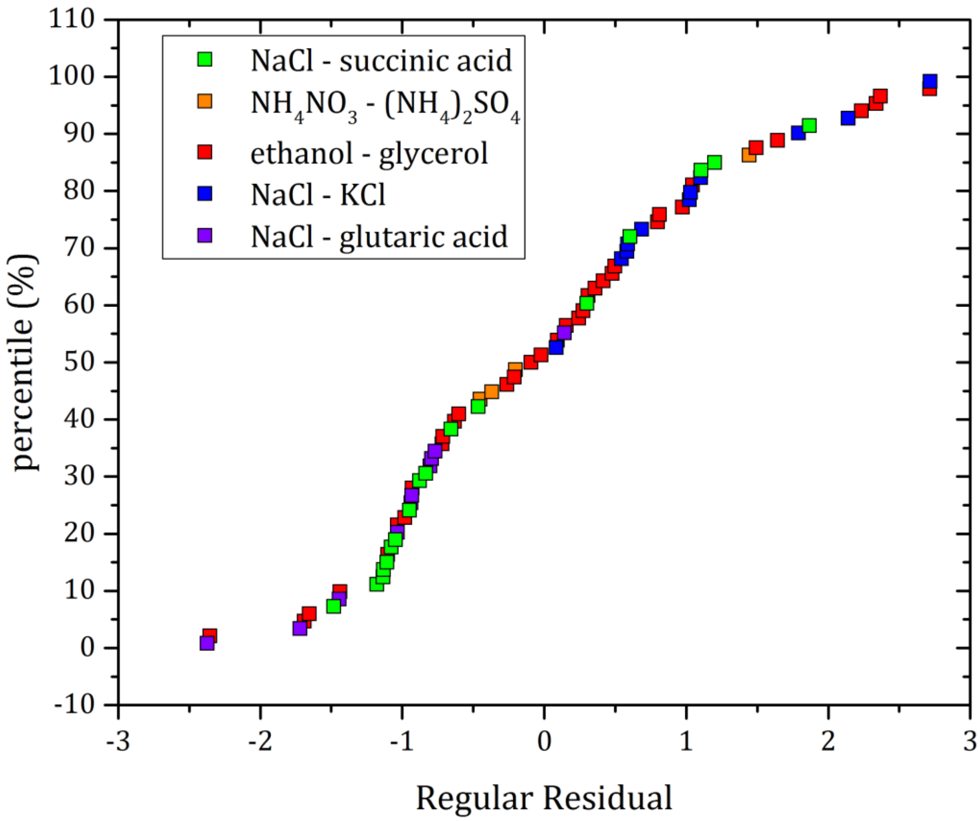

Figure S2: Regular residuals and their percentiles for all systems studied.

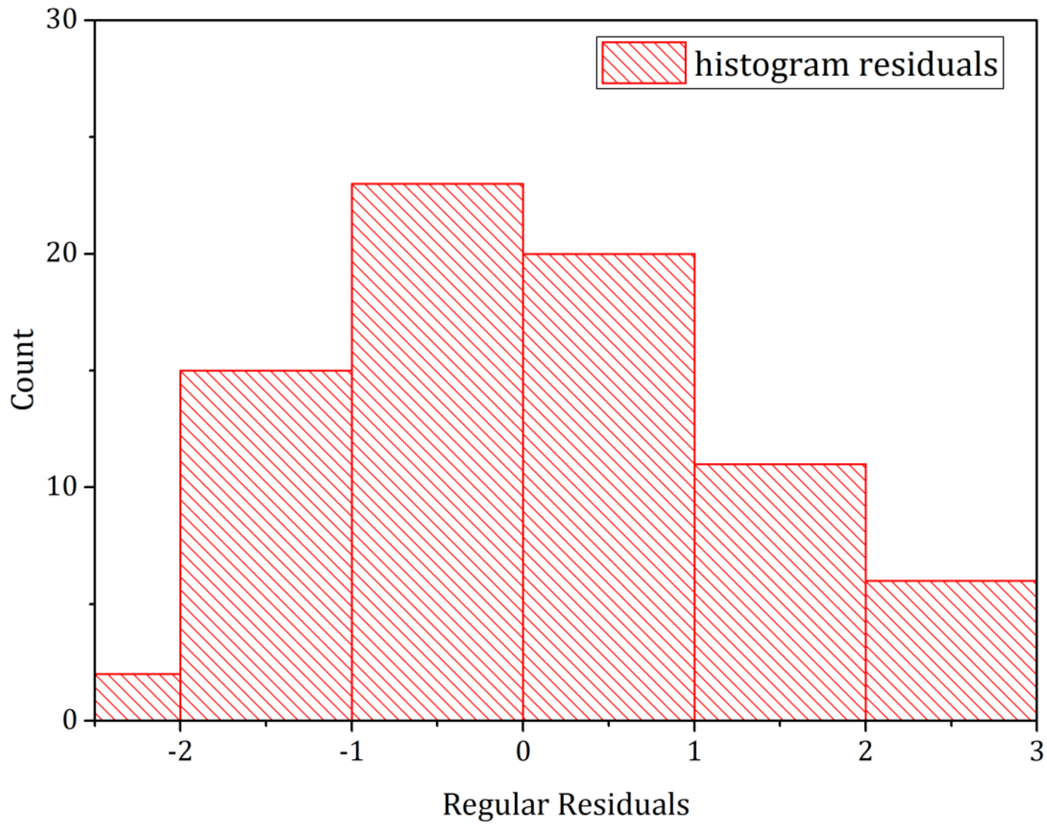

Figure S3: Histogram plot of regular residuals for all systems studied in this work.

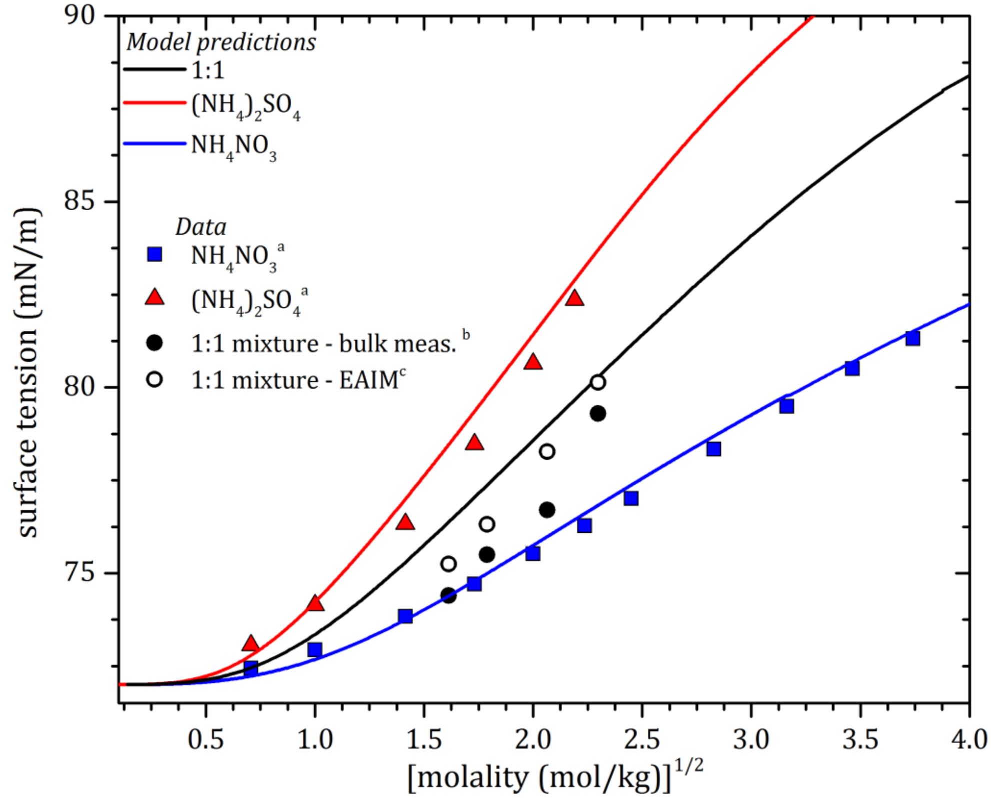

Figure S4: Surface tension model predictions and measurements vs. square root of molality for the ternary system consisting of NH_4NO_3 (AN) and $(NH_4)_2SO_4$ (AS) mixtures in aqueous solutions. The plot is similar to Figure 5 in the manuscript, except 3 model parameters are used to parametrize AS and 1 parameter for AN. Data sources: [a]ammonium nitrate and ammonium sulfate (Washburn et al,1928[39]), [b]1:1 mole ratio (measured with Digital Tensiometer K10ST by Krüss).