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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

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

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

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

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

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

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

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

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

$$K_j a_j = 1 - \frac{N_{jS}}{N_j} \quad (S5)$$

where $K_j = \exp\left(\frac{\Delta\varepsilon_{jB}}{k_B T}\right)$. 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

$$\begin{aligned} C_j &= \exp\left(\frac{\Delta\varepsilon_{jS}}{k_B T}\right) \\ &= \prod_{k < j} \prod_{l < k} \dots \frac{N_{jS}^2}{N_j - N_{jS}} \left\{ \left(\frac{r_j}{N_{WS} - r_j N_{jS}} \right)^{(n-1)!} \left(\frac{r_j}{N_{WS} - r_j N_{jS} - r_k N_{kS}} \right)^{(n-2)!} \right. \\ &\quad \times \left(\frac{r_j}{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}} \right)^{(n-3)!} \\ &\quad \times \left(\frac{N_{WS} - r_j N_{jS}}{N_{WS} - r_j N_{jS} - r_k N_{kS}} \right)^{(n-2)! r_j / r_k} \\ &\quad \times \left(\frac{N_{WS} - r_j N_{jS} - r_k N_{kS}}{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}} \right)^{(n-3)! r_j / r_l} \\ &\quad \times \left(\frac{N_{WS} - r_j N_{jS} - r_k N_{kS}}{r_k} \right)^{(n-3)! r_j / r_l} \\ &\quad \left. \times \left(\frac{r_l}{N_{WS} - r_j N_{jS} - r_k N_{kS} - r_l N_{lS}} \right)^{(n-3)! r_j / r_l} \right\}^{\frac{1}{n!}} \end{aligned} \quad (S6)$$

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

$$\begin{aligned} \sigma &= \sigma_w \\ &+ \sum_{j=A}^Z \sum_{k < j} \sum_{l < k} \dots \frac{kT}{r_j S_w} \frac{1}{n!} \text{Ln} \left(\left(\frac{N_{WS} - r_j N_{js}}{N_{WS}} \right)^{(n-1)!} \left(\frac{r_j (N_{WS} - r_j N_{js} - r_k N_{ks})}{r_k (N_{WS} - r_k N_{ks})} \right)^{(n-2)!} \right. \\ &\quad \left. \left(\frac{r_j (N_{WS} - r_j N_{js} - r_k N_{ks} - r_l N_{ls})}{r_l (N_{WS} - r_k N_{ks} - r_l N_{ls})} \right)^{(n-3)!} \dots \right) \end{aligned} \quad (S7)$$

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)
$n=1$	$N_A \ln \left(\frac{N_A}{N_A - N_{AS}} \right) + \frac{N_{WS}}{r_A} \left(\frac{N_{WS}}{N_{WS} - r_A N_{AS}} \right) + \frac{(N_{WS} - r_A N_{AS})(N_A - N_{AS})}{r_A N_{AS}^2}$
$n=2$	$ \begin{aligned} & 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} \end{aligned} $

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

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, $\text{NH}_4\text{NO}_3 - (\text{NH}_4)_2\text{SO}_4$ (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 $(\text{NH}_4)_2\text{SO}_4$ (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: ^aammonium nitrate and ammonium sulfate (Washburn et al,1928³⁹), ^b1:1 mole ratio (measured with Digital Tensiometer K10ST by Krüss).