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Parameter Interpretation and Reduction for a Unified Statistical Mechanical Surface Tension Model

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Supporting Information

ABSTRACT: Surface properties of aqueous solutions are important for environments as diverse as atmospheric aerosols and biocellular membranes. Previously, we developed a surface tension model for both electrolyte and nonelectrolyte aqueous solutions across the entire solute concentration range (Wexler and Dutcher, J. Phys. Chem. Lett. 2013, 4, 1723–1726). The model differentiated between adsorption of solute molecules in the bulk and surface of solution using the statistical mechanics of multilayer sorption solution model of Dutcher et al. (J. Phys. Chem. A 2013, 117, 3198–3213). The parameters in the model had physicochemical interpretations, but remained largely empirical. In the current work, these parameters are related to solute molecular properties in aqueous solutions. For nonelectrolytes, sorption tendencies suggest a strong relation with molecular size and functional group spacing. For electrolytes, surface adsorption of ions follows ion surface-bulk partitioning calculations by Pegram and Record (J. Phys. Chem. B 2007, 111, 5411–5417).

Predictive models of surface tension as a function of solute concentration are vital to numerous environmental, biological, and industrial processes. In atmospheric aerosol sciences, for example, models of surface tension are needed in order to predict homogeneous nucleation, growth of these nanoparticles to cloud condensation nuclei (CCN), activation of CCN to clouds, aerosol particle morphology, and other aerosol properties that influence weather, climate, and health. However, atmospheric aerosol microenvironments are composed of highly complex chemical solutions, comprising both electrolytes and organic compounds. Limited composition data for aerosol particles are available from a combination of field and laboratory measurements1−5 and model predictions,6−8 yielding only indicators of the organic composition (e.g., oxygen to carbon ratios, structural groups present).7,8 The challenge for models of surface tension relevant to atmospheric particles is predicting surface tension from only indications of composition.

There has been extensive research in the literature relating surfactant properties of molecules to their group composition and structure. Quantitative structure property relationships (QSPR) for surfactants have been employed to relate properties of molecules to pure compound surface tension, the critical micelle concentration, the cloud point, and hydrophilic–lipophilic balance.9 These correlations use a few key molecular properties such as the Kier and Hall zeroth-order connectivity index,10 the second-order structural information index,11 the relative number of oxygen and nitrogen atoms (relevant to the surface activity of amines and related compounds), and the dipole moment.12 These correlations and others suggest that simple relationships may exist between surface tension and organic compound moieties in atmospheric particles and other applications.

Recently, Wexler and Dutcher13 used statistical mechanics of multilayer sorption to develop a surface tension model where the surface sorbs a single layer of solute molecules. This model was successful over the full range of concentrations from pure solvent to pure solute, and worked equally well for organics and electrolytes in aqueous solutions. Therefore, the model has important implications for many fields, where surface properties are important over a large concentration range. The goal of the current work is to identify model parameter values for a breadth of solutes, relate them to solute physical properties, and demonstrate a parameter free, fully predictive surface tension model for single solute aqueous solutions. Literature values for surface tension (see Wang et al, 201114 for one compendium) and solute molecular properties are used to develop relationships for the parameters in the Wexler and Dutcher surface tension model.

Methods. Wexler and Dutcher13 employ statistical mechanics to derive an expression that relates solution surface tension to solute activity. An expression for the Gibbs free energy, G ≈ E – TS, was derived, where the energy term includes solute molecular energies in the surface and bulk, and the entropy is found from Boltzmann’s formula, S = kLnΩ, and partition functions for surface and bulk. In this framework, the Gibbs dividing surface is implicitly defined by assuming single-layer adsorption is sufficient to describe the surface tension as a function of composition. Evaluating the system in the limit of...
pure solvent gives the surface tension of the solvent alone, assumed to be water in this work (\(\sigma_w\)). The solution surface tension was found to be

\[
\sigma = \sigma_w + \frac{kT}{rS_w} \ln \left( \frac{1 - K \alpha_k}{1 - K \alpha_k(1 - C)} \right)
\]

(1)

where \(k\) is Boltzmann’s constant, \(T\) is temperature, \(S_w\) is the surface area occupied by one solvent molecule, and \(\alpha_k\) is the solute activity. The remaining quantities (\(r, K, C\)) are model parameters, where \(r\) is the average number of water molecules each solute molecule displaces from the surface, and \(K\) and \(C\) are related to the sorption energies. Specifically, \(K \equiv \exp(\varepsilon_{SB}/kT)\) and \(C \equiv \exp(\varepsilon_{SS}/kT)\), where \(\varepsilon_{SB}\) and \(\varepsilon_{SS}\) are the energies of each solute molecule in the bulk and surface, respectively.

Wang and co-workers also developed a single solute surface tension model as a function of solute activity. Equation 1 can be rearranged to \(\sigma = \sigma_w - (kT/rS_w) \ln[1 + K \alpha_k/(1 - K \alpha_k)]\), comparable to eq 13 of the Wang model, \(\sigma = \sigma_w + kT \exp(\varepsilon_{SB}/kT) \ln[1 - K \alpha_k/(1 + K \alpha_k)]\), in which \(K\) has the same meaning in both models, and surface excess \(\Gamma\) has a similar role to \(r\) in eq 1. Note that the Wang model does not use an equilibrium solute partitioning \(C\) parameter.

Pegram and Record developed a thermodynamic analysis that treats individual ionic contributions to surface tension increments (their eq 1 and 3) for dilute aqueous electrolyte solutions. Separating single ion effects leads to their calculation of ion solute-bulk partitioning and, by addition, electrolyte partition coefficients, denoted as \(K_p\). It will be shown in this work that \(K_p\) strongly correlates with the \(C\) parameter in our model, which represents equilibrium partitioning of the solute between surface and bulk.

Equation 1 can be solved for pure solute obtaining an expression for \(C\) in terms of the pure solvent and solute (\(\sigma_s\)) surface tensions:

\[
C = 1 - \frac{1 - (1 - K) \exp[(\sigma_w - \sigma_s) * rS_w/kT]}{K}
\]

(2)

which can be used to eliminate one of the three free parameters from eq 1 when pure solute surface tension is known. For liquid solutes, such as many liquid organics, solute surface tension data are widely available. For electrolyte salts, most of which are solid at 298 K, \(\sigma_s\) values can be predicted using the method described in Dutcher and co-workers by extrapolating high-temperature molten salt surface tension to 298 K using a slope and intercept based on melting temperature, cation radius, and molar volume.

As shown by Weder and Dutcher, eq 1 has a limiting case for compounds where partitioning to the surface is strongly preferred, such as alcohols, for which \(\varepsilon_{SB} \to -\infty\) causing \(K \to 0\). In this case, eq 1 reduces to

\[
\sigma = \sigma_w - \frac{kT}{rS_w} \ln(1 + K' \alpha_k)
\]

(3)

a form of the Szyszkowski equation. If the pure solute and solvent surface tensions are known, parameter \(K'\) can be found by evaluating eq 3 in the limit of \(\alpha_k \to 1\).

\[
\ln(K' + 1) = \frac{rS_w(\sigma_w - \sigma_s)}{kT}
\]

(4)

leaving \(r\) as the single fit parameter. In this work, solute activity values, \(\alpha_k\), in the above equations were calculated from solute activity or molality data using the solution thermodynamics model of Dutcher and co-workers, who extended the monolayer adsorption isotherms of Brunauer–Emmett–Teller (BET), Guggenheim–Anderson–deBoer (GAB), and Ally and Braunstein to multiple monolayer formulation.

The surface tension model fit parameter values are identified by minimizing the root mean squared error, \(\text{RMSE} = (\sum_i (\sigma_{\text{fit}} - \sigma_{\text{exp}})^2/n_p)^{1/2}\), where \(n_p\) is the number of data points in the fit.

Organics. Surface tension predictions using eq 1 or 3 are shown in Figure 1 for representative aqueous solutions containing water-soluble organic compounds (see Supporting Information for organics not shown in this figure). In the dilute range, surface tension depression is clearly steeper for surface active compounds that displace more waters from the surface reflected in larger values of the model parameter \(r\). For example, refer to Table 1, \(r = 2.58, 3.00,\) and \(4.56\) for methanol, ethanol, and isopropanol, respectively, showing an increase in value with the number of methyl groups. Since methyl groups increase molecular volume, it is expected that \(K'\), a function of \(r\) through eq 3, depends on solute volume. Figure 2 shows the relationship between \(K'\) and solute molar volume \(v\) for simple alcohols with one hydroxyl group (black squares) and glycols with two hydroxyl groups (blue circles). Size dependence is observed for both classes of alcohols because of the competing effects from hydroxyl groups increasing bulk solubility and methyl groups increasing surface preference. A regression following the functional form of eq 4 gives \(\ln(K' + 1) = 0.067v\).

Combining eqs 3 and 4 to eliminate \(r\) gives

\[
\sigma = \sigma_w - (\sigma_w - \sigma_s) \ln(1 + K' \alpha_k) \quad \ln(1 + K')
\]

(5)

Figure 1. Surface tension as a function of solute activity for methanol, 1,2 ethanediol (also known as monoethylene glycol), and 1,3 butanediol. The label \(n_m\) represents the number of adjustable parameters. The lines with two fit parameters are eq 1 (red dashed line, \(n_m = 2\)); the one-parameter curves are eq 3 (dark yellow dashed-dotted line, \(n_m = 1\)); and the parameter-free line is eq 5 (blue solid line, \(n_m = 0\)), using the relationship between \(K'\) and alcohol molar volume in Figure 2. Data information is given in Table 1.
Table 1. Summary of Model Parameters and Data References for Organic Substances

<table>
<thead>
<tr>
<th>solute</th>
<th>r (fit)</th>
<th>(K') (calc)</th>
<th>(\sigma)</th>
<th>(C_{\text{obs}})</th>
<th>RMSE</th>
<th>(n_p)</th>
<th>(x_{\text{max}})</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>2.58</td>
<td>22.32</td>
<td>22.0</td>
<td>-</td>
<td>1.21</td>
<td>14/1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td>3.00</td>
<td>69.19</td>
<td>22.2</td>
<td>-</td>
<td>3.48</td>
<td>15/1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>isopropanol</td>
<td>4.3</td>
<td>291.2</td>
<td>21.0</td>
<td>-</td>
<td>2.74</td>
<td>14/1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1,2 ethanediol</td>
<td>6.42</td>
<td>57.79</td>
<td>46.2</td>
<td>-</td>
<td>0.341</td>
<td>18/1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1,2 propanediol</td>
<td>5.82</td>
<td>173.6</td>
<td>35.5</td>
<td>-</td>
<td>1.88</td>
<td>18/1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1,3 propanediol</td>
<td>8.28</td>
<td>156.8</td>
<td>47.0</td>
<td>-</td>
<td>0.986</td>
<td>18/1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1,3 butanediol</td>
<td>6.77</td>
<td>326.7</td>
<td>37.0</td>
<td>-</td>
<td>1.24</td>
<td>18/1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1,4 butanediol</td>
<td>7.47</td>
<td>322.6</td>
<td>43.8</td>
<td>-</td>
<td>0.816</td>
<td>18/1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>sorbitol</td>
<td>20.3</td>
<td>334.4</td>
<td>60.2</td>
<td>-</td>
<td>0.197</td>
<td>7/0.041</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>glycerol</td>
<td>33.1</td>
<td>0.91</td>
<td>62.0</td>
<td>-</td>
<td>331.7</td>
<td>0.0969</td>
<td>11/1</td>
<td></td>
</tr>
<tr>
<td>sucrose</td>
<td>−34.7</td>
<td>0.99</td>
<td>121</td>
<td>2.932</td>
<td>0.0468</td>
<td>5/0.16</td>
<td>27</td>
<td></td>
</tr>
</tbody>
</table>

The activity sources are from adsorption isotherm DGWC, with energy of multilayer adsorption parameters derived by a power law fit for glycerol and Coulombic potential interaction for the rest of the solutes. The limiting case fit eq 3, and a single adjustable parameter, \(r\), was used for all compounds except sorbitol, glycerol, and sucrose. For all eq 3 fits, the value of \(K'\) was obtained with eq 4. For glycerol, the full form of the model eq 1 was used, with \(r\) and \(K\) as adjustable parameters. For sucrose, the full model (eq 1) was used, with \(r\), \(K\), and \(\sigma\) as adjustable parameters. A calculated value for \(C\) is supplied for both full model eq 1 cases. Number of data points, \(n_p\), given in listed reference (ref.), with a maximum mole fraction, \(x_{\text{max}}\). For sorbitol, the pure solute surface tension is not known, so the limiting case eq 3 fit was used with 2 parameters, \(r\) and \(\sigma\). Methanol surface tension measurements were taken by the author with a Wilhemy plate method.

Equation 2 can be used to replace the remaining parameter, \(r\), with the parameter \(C\). Figure 3 shows the relationship between \(C\) and the partitioning coefficients \(K_p\) of Pegram and Record. An important physical observation from this trend is that the propensity of specific ions to adsorb at the surface is dominated by anions, as shown by the clearly grouped electrolyte species in Figure 3. Also, a series of anion families emerges in order of most to least surface active, beginning with nitrates, followed by chlorides then sulfates. The regression in Figure 3 is \(C = (2.878 \times 10^5) \exp(-14.0K_p)\). Combining eqs 1 and 2 to eliminate \(r\) gives

\[
\sigma = \sigma_w - (\sigma_s - \sigma_w) \left( \frac{1}{1 - Ka} \right) \frac{\ln \left( \frac{1}{1 - Ka(1 - C)} \right)}{\ln \left( \frac{1}{1 - K(1 - C)} \right)}
\]

Equation 6 reduces to eq 5 for \(C = 1\). Using \(K = 0.99\) and the regression above for \(C\) as a function of \(K_p\) in eq 6 produces a parameter-free model that is fully predictive. Results of reduction to double parameter \((r\) and \(K)\), single parameter

![Figure 2](image_url)  
**Figure 2.** \(\ln(K' + 1)\) as a function of molar volume for alcohols with two hydroxyl groups (blue circles) and one hydroxyl group (black squares). The linear regression is \(\ln(K' + 1) = 0.067v\).

![Figure 3](image_url)  
**Figure 3.** \(C\) versus partitioning coefficient \(K_p\) from Pegram and Record. \(C\) values are found using an estimate for \(\sigma\) from Dutcher et al. and constant \(K = 0.99\), leaving \(r\) as the only adjustable parameter. The exponential regression is \(C = (2.878 \times 10^5)e^{-14.0K_p}\).
Table 2. Summary of Model Parameters Resulting from Electrolyte Fits Using Eq 1 Following Parameter Reduction and Data References for Aqueous Electrolyte Solutions

<table>
<thead>
<tr>
<th>solute</th>
<th>$n_m = 2$ (eq 1)</th>
<th>$n_m = 1$ (eq 1)</th>
<th>$n_m = 0$ (eq 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>$r$ (fit)</td>
<td>$K$ (fit)</td>
<td>RMSE</td>
</tr>
<tr>
<td>KCl</td>
<td>-4.78</td>
<td>0.99</td>
<td>1.59</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>-3.64</td>
<td>0.99</td>
<td>0.834</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>-3.28</td>
<td>0.99</td>
<td>0.407</td>
</tr>
<tr>
<td>RbCl</td>
<td>-3.72</td>
<td>0.99</td>
<td>0.932</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>-5.52</td>
<td>0.99</td>
<td>0.493</td>
</tr>
<tr>
<td>KNO₃</td>
<td>-3.84</td>
<td>0.99</td>
<td>0.120</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>-6.74</td>
<td>0.99</td>
<td>0.146</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>-3.51</td>
<td>0.97</td>
<td>0.280</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>-4.04</td>
<td>0.99</td>
<td>0.999</td>
</tr>
</tbody>
</table>

**Notes:**

- For $n_m = 2$, an estimated value for $\sigma_s$ from ref 16 was used to eliminate an adjustable parameter. For $n_m = 1$, the average value $K = 0.99$ was used for all electrolytes while $r$ was allowed to vary. For $n_m = 0$, the model inputs are pure solute surface tension estimates and partition coefficients by Pegram and Record.$^{15}$ The activity sources are all from adsorption isotherms.$^{18–20}$ For the sulfates and CaCl₂, activity parameters are derived from a power law fit; for all other species, the energy of multilayer adsorption parameters are derived from Coulombic interactions.$^{36}$ Number of data points, $n_p$, given in listed reference (ref.), with a maximum molality, $m_{max}$, in kg/mol. Data was taken from both ref 27 and by the author via Wilhelmy plate method.

$^a$For $n_m = 2$, an estimated value for $\sigma_s$, from ref 16 was used to eliminate an adjustable parameter. For $n_m = 1$, the average value $K = 0.99$ was used for all electrolytes while $r$ was allowed to vary. For $n_m = 0$, the model inputs are pure solute surface tension estimates and partition coefficients by Pegram and Record.$^{15}$ The activity sources are all from adsorption isotherms.$^{18–20}$ For the sulfates and CaCl₂, activity parameters are derived from a power law fit; for all other species, the energy of multilayer adsorption parameters are derived from Coulombic interactions.$^{36}$ Number of data points, $n_p$, given in listed reference (ref.), with a maximum molality, $m_{max}$, in kg/mol. Data was taken from both ref 27 and by the author via Wilhelmy plate method.

$^b$Parameter fit in which $K$ is held at 0.99, the standard error for $r$ is 0.0557, a significant decrease from the two-parameter fit. Similarly, for $(\text{NH}_4)_2\text{SO}_4$, standard errors for $r$ and $K$ are 1.68 and 0.428, and for just $r_0$, 0.267. For NH₄Cl, standard errors for $r$ and $K$ are 3.75 and 1.30, and for just $r$, 0.24. In general, the RMSE values reported in Tables 1 and 2 are on the order of magnitude of 0.1 to 1.0 mN/m. The literature sources report errors no greater in magnitude than 0.1 mN/m. For example, Yazquez et al.$^{26}$ reports a maximum experimental error of ±0.4% mN/m after averaging 5–10 measurements. Also, the International Critical Tables$^{27}$ typically report standard deviations of ±0.1 mN/m.

**Summary.** A model of surface tension as a function of solute activities was applied to electrolytes and organic aqueous solutions. Solute concentrations were converted from molalities to activities using the adsorption isotherm model of Dutcher et al.$^{8–20}$ Surface tension as a function of activity is given by eq 1 for both organic and electrolyte solutions, and requires three model parameters: $r$, $K$, and $\sigma_s$.

For the organics considered in this study, except glycerol and sucrose, a form of the Szyszkowski equation,$^{17}$ eq 3, was used. The Szyszkowski equation, a limiting case of the full model where the solute primarily resides on the surface, requires only two free parameters, $K'$ and $\sigma_s$. Since $\sigma_s$ is known for many liquid organics, only a single model parameter, $K'$, is needed for this limiting case. We showed that a simple relationship between the model parameter $K'$ and the molar volume $\nu$ of the pure solute provides reasonably accurate estimates for surface tension as a function of solute activity, given in eq 5.

For binary electrolytes, the full model, eq 1, which requires three parameters, was applied to all electrolyte species represented in this work, including sulfates, nitrates, and chlorides. Estimates of pure solute surface tension, $\sigma_s$, from Dutcher et al.$^{18}$ at 298 K were used to replace that parameter. Next, evaluation of many electrolytes suggested that $K$ could be considered a constant with a value of 0.99 reducing the number of model parameters to one. To obtain a parameter-free model for electrolytes, partitioning coefficient $K'$ from Pegram and Record$^{15}$ was compared to our results for C, eliminating the final parameter. The reduced-parameter model for surface tension of binary electrolyte solutions is given in eq 6.

**Figure 4.** Surface tension as a function of electrolyte activity for ammonium sulfate, ammonium chloride, and ammonium nitrate. For all curves, pure solute surface tension ($\sigma_s$) predictions were obtained from ref 16. The red dashed line is eq 1, using parameters $r$ and $K$. The dark yellow dash-dot line is also eq 1, keeping $K$ as a constant equal to 0.99 and allowing $r$ to vary. The blue solid lines are parameter free fits with eq 6, where $C$ is from the regression curve from Figure 3. Shown in the subplot are data points with surface tension curves in the limited ranges up to the solubility limit for each species. Data references are summarized in Table 2.
The model of Wexler and Dutcher was derived from fundamental statistical mechanics considerations and was shown in that work to accurately represent the surface tension-activity relationship over the full range of concentrations from pure solvent to pure solute. That model had two or three parameters, depending on the nature of the solute. In this work we related these parameters to properties of the solute in aqueous solution to increase the predictive capabilities of the model for compounds with insufficient data. The predictive surface tension models developed here will have important implications for fundamental thermodynamic studies of specific ion attraction or repulsion from the surface and surface forces produced by image charges and ion hydration, as well as in crucial applications ranging from desalination of water to atmospheric aerosol particle dynamics modeling.

■ ASSOCIATED CONTENT

1 Supporting Information
Additional plots showing surface tension predictions of solutes given in Tables 1 and 2 that do not appear in either Figures 1 or 4. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.5b01346. (PDF)

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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