Title

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

Journal
The Journal of Physical Chemistry Letters, 6(17)

ISSN
1948-7185

Authors

Boyer, Hallie
Wexler, Anthony
Dutcher, Cari S

Publication Date
2015-09-03

DOI
10.1021/acs.jpclett.5b01346

Peer reviewed

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

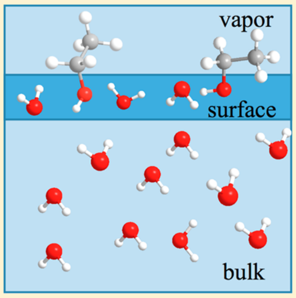
Parameter Interpretation and Reduction for a Unified Statistical Mechanical Surface Tension Model

Hallie Boyer,[†] Anthony Wexler,[‡] and Cari S. Dutcher*[,†]

[†]Department of Mechanical Engineering, University of Minnesota, Twin Cities, Minneapolis, Minnesota 55455, United States
[‡]Air Quality Research Center, University of California, Davis, California 95616, United States

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 measurements[1−4] and model predictions,[5,6] 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 Dutcher[13] 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, 2011[14] 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 Dutcher[13] employ statistical mechanics to derive an expression that relates solution surface tension to solute activity. An expression for the Gibbs free energy, $G \approx E - TS$, was derived, where the energy term includes solute molecular energies in the surface and bulk, and the entropy is found from Boltzmann's formula, $S = kLn\Omega$, 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

Received: June 24, 2015
Accepted: July 30, 2015
Published: July 30, 2015

DOI: 10.1021/acs.jpclett.5b01346
J. Phys. Chem. Lett. 2015, 6, 3384−3389

pure solvent gives the surface tension of the solvent alone, assumed to be water in this work (σ_W). The solution surface tension was found to be

$$\sigma = \sigma_W + \frac{kT}{rS_W} \ln\left(\frac{1 - Ka_S}{1 - Ka_S(1 - C)}\right) \tag{1}$$

where k is Boltzmann's constant, T is temperature, S_W is the surface area occupied by one solvent molecule, and a_S is the solute activity. The remaining quantities (r, K, and 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 $C \equiv \exp((\varepsilon_{SS} - \varepsilon_{SB})/kT)$, where ε_{SB} and ε_{SS} are the energies of each solute molecule in the bulk and surface, respectively.

Wang and co-workers[14] also developed a single solute surface tension model as a function of solute activity. Equation 1 can be rearranged to $\sigma = \sigma_W - (kT/rS_W) \ln[1 + KCa_S/(1 - Ka_S)]$, comparable to eq 13 of the Wang model, $\sigma = \sigma_W + kT\Gamma^{\sigma,0} \ln[1 - Ka_s/(1 + Ka_s)]$, in which K has the same meaning in both models, and surface excess $\Gamma^{\sigma,0}$ 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[15] developed a thermodynamic analysis that treats individual ionic contributions to surface tension increments (their eqs 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 (σ_S) surface tensions:

$$C = 1 - \frac{[1 - (1 - K) \exp\{(\sigma_W - \sigma_S)^* rS_W/kT\}]}{K} \tag{2}$$

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, σ_S values can be predicted using the method described in Dutcher and co-workers[16] 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 Wexler and Dutcher,[13] eq 1 has a limiting case for compounds where partitioning to the surface is strongly preferred, such as alcohols, for which $\varepsilon_{SB} \rightarrow -\infty$ causing $K \rightarrow 0$. In this case, eq 1 reduces to

$$\sigma = \sigma_W - \frac{kT}{rS_W} \ln(1 + K'a_S) \tag{3}$$

a form of the Szyszkowski equation.[17] If the pure solute and solvent surface tensions are known, parameter K' can be found by evaluating eq 3 in the limit of $a_s \rightarrow 1$.

$$\ln(K' + 1) = \frac{rS_W(\sigma_W - \sigma_S)}{kT} \tag{4}$$

leaving r as the single fit parameter. In this work, solute activity values, a_S, in the above equations were calculated from solvent activity or molality data using the solution thermodynamics model of Dutcher and co-workers,[18−20] who extended the monolayer adsorption isotherms of Brunauer−Emmett−Teller (BET),[21] Guggenheim−Anderson−deBoer (GAB),[22−24] and Ally and Braunstein[25] to multiple monolayer formulation.

The surface tension model fit parameter values are identified by minimizing the root mean squared error, RMSE = $(\sum_1^{n_P}(\sigma_{\text{fit}} - \sigma_{\text{data}})^2/n_P)^{1/2}$, 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

$$\sigma = \sigma_W - (\sigma_W - \sigma_S)\frac{\ln(1 + K'a_S)}{\ln(1 + K')} \tag{5}$$

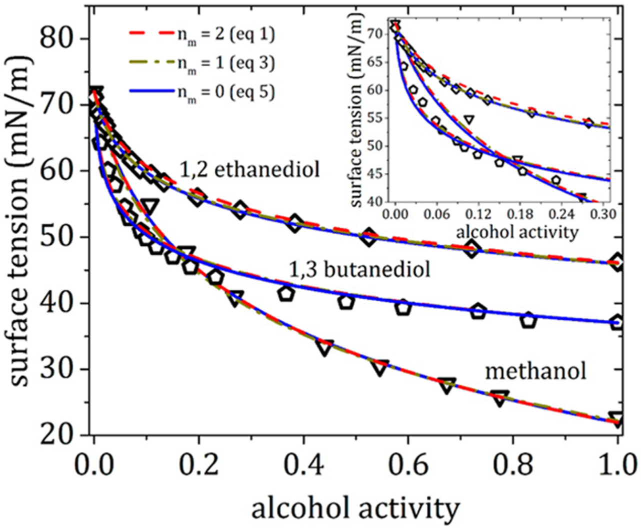


Figure 1. Surface tension as a function of solute activity for methanol, 1,2 ethanediol (also known as monoethylenge glycol), and 1,3 butanediol. The label "n_m" represents the number of adjustable parameters. The lines with two fit parameters are eq 1 (red dashed line, n_m = 2); the one-parameter curves 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[a]

solute	r (fit)	K' (calc)	σ_s	$C^{b,c}$	RMSE	n_P[d]	x_{max}[d]	ref[d]
methanol	2.58	22.32	22.0	-	1.21	14[f]	1	-
ethanol	3.00	69.19	22.2	-	3.48	15	1	26
isopropanol	4.3	291.2	21.0	-	2.74	14	1	26
1,2 ethanediol	6.42	57.79	46.2	-	0.341	18	1	33
1,2 propanediol	5.82	173.6	35.5	-	1.88	18	1	33
1,3 propanediol	8.28	156.8	47.0	-	0.986	18	1	33
1,3 butanediol	6.77	326.7	37.0	-	1.24	18	1	33
1,4 butanediol	7.47	322.6	43.8	-	0.816	18	1	33
sorbitol[e]	20.3	334.4	60.2	-	0.197	7	0.041	34
glycerol[b]	33.1	0.91	62.0	331.7	0.0969	11	1	35
sucrose[c]	−34.7	0.99	121	2.932	0.0468	5	0.16	27

[a] The activity sources are from adsorption isotherm DGWC,[18−20] with energy of multilayer adsorption parameters derived by a power law fit for glycerol and Coulombic potential interaction[36] 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. [b] For glycerol, the full form of the model eq 1) was used, with r and K as adjustable parameters. [c] For sucrose, the full model (eq 1) was used, with r, K, and σ_s as adjustable parameters. A calculated value for C is supplied for both full model eq 1 cases. [d] Number of data points, n_P, given in listed reference (ref.), with a maximum mole fraction, x_{max}. [e] For sorbitol, the pure solute surface tension is not known, so the limiting case eq 3 fit was used with 2 parameters, r and σ_s. [f] Methanol surface tension measurements were taken by the author with a Wilhemy plate method.

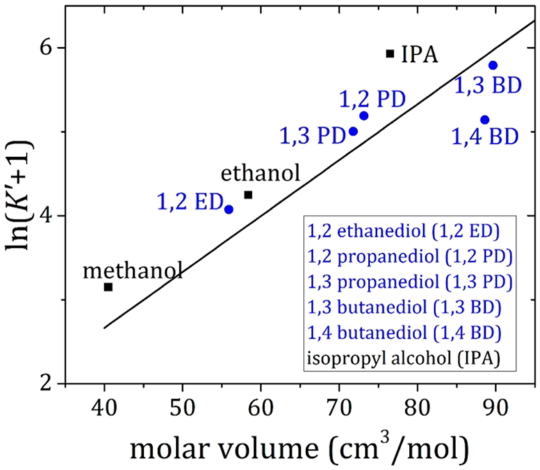


Figure 2. $\ln(K' + 1)$ as a function of molar volume for alcohols with two hydroxyl groups (blue circles) and one hydroxyl group (black squares). The linear regression is $\ln K' + 1 = 0.067v$.

Since K' is only a function of v, eq 5 is a parameter-free model of surface tension for certain organic solutes as long as the pure solute surface tension and specific volume are known. Figure 1 shows excellent agreement among three treatments: the full model (eq 1) with two fit parameters, the limiting case model (eq 3) with one fit parameter, and the volume-based model (eq 5) with no fit parameters.

Electrolytes. Whereas the surface tension of many surface active organics in aqueous solutions can be modeled by eq 3, the full three parameter model eq 1 is needed for predicting surface tension for electrolyte solutions. In eqs 1 and 2, there are three independent variables among r, K, C, and σ_S. A hypothetical value of pure solute surface tension, σ_S, at 298 K can be estimated using the methods of Dutcher et al.,[16] thereby eliminating a parameter. Fitting r and K with the aqueous electrolyte surface tension data yields values of K similar for nearly all electrolytes addressed here. By treating K as a constant equal to 0.99, r is the only remaining fit parameter. For comparison, the values of K' for surface active organics are in the range of 30 to 200 since they partition to the surface much more readily than the electrolytes.

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.[15] 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

$$\sigma = \sigma_W - (\sigma_S - \sigma_W)\frac{\ln\left(\frac{1 - Ka_S}{1 - Ka_S(1 - C)}\right)}{\ln\left(\frac{1 - K}{1 - K(1 - C)}\right)} \qquad (6)$$

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

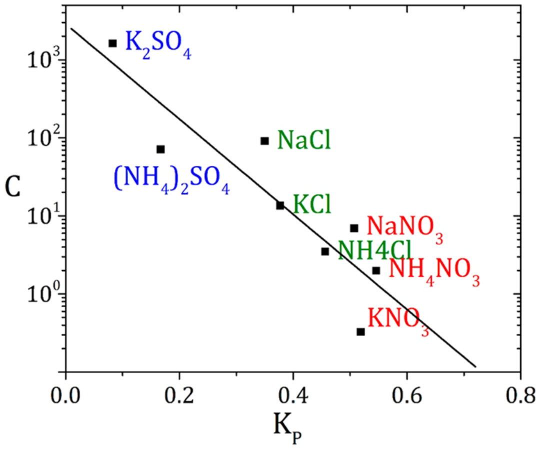


Figure 3. C versus partitioning coefficient K_P from Pegram and Record.[15] C values are found using an estimate for σ_S from Dutcher et al.[16] and constant $K = 0.99$, leaving r as the only adjustable parameter. The exponential regression is $C = (2.878 \times 10^5)e^{-14.0K_P}$.

DOI: 10.1021/acs.jpclett.5b01346
J. Phys. Chem. Lett. 2015, 6, 3384−3389

Table 2. Summary of Model Parameters Resulting from Electrolyte Fits Using Eq 1 Following Parameter Reduction and Data References for Aqueous Electrolyte Solutions[a]

	n_m = 2 (eq 1)			n_m = 1 (eq 1)		n_m = 0 (eq 6)			
solute	r (fit)	K (fit)	RMSE	r (fit)	RMSE	RMSE	n_P[b]	m_{max}[b]	ref.[b]
NaCl	−4.78	0.99	1.59	−4.78	1.58	3.56	22[c]	6	27
KCl	−4.77	0.99	0.594	−4.76	0.559	0.559	12	14	27
NH_4Cl	−3.64	0.99	0.834	−3.64	0.844	0.794	7	8	27
$CaCl_2$	−32.8	0.99	0.407	-	-	-	10	7	37
RbCl	−3.72	0.99	0.932	−3.72	0.926	-	12	6.9	38
$NaNO_3$	−5.52	0.99	0.493	−5.52	0.493	2.49	15	14	27
KNO_3	−3.84	0.99	0.120	−3.84	0.120	3.60	7	3.6	38
NH_4NO_3	−6.74	0.99	0.146	−6.82	0.146	1.03	12	12	27
K_2SO_4	−3.51	0.97	0.280	−3.88	0.285	0.436	13	4.8	37
$(NH_4)_2SO_4$	−4.04	0.99	0.999	−4.04	0.999	2.57	7	14	27

[a] For n_m = 2, an estimated value for σ_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 $CaCl_2$, 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] [b] Number of data points, n_P, given in listed reference (ref.), with a maximum molality, m_{max} in kg/mol. [c] Data was taken from both ref 27 and by the author via Wilhemy plate method.

(r), and zero parameter versions of the model are summarized in Table 2.

Representative electrolyte results for surface tension predictions of ammonium aqueous solutions are found in Figure 4, using the full model with pure electrolyte surface tension predictions from ref 16 (eq 1, n_m = 2), further reduced model with K as a constant (eq 1, n_m = 1), and finally a parameter-free model based on calculated partitioning coefficients from ref 15 (eq 6, n_m = 0). Uncertainty of model parameters decreased through parameter reduction. For NH_4NO_3, standard errors for r and K in the two parameter treatment are 0.621 and 0.138, respectively; for the single 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 $(NH_4)_2SO_4$, standard errors for r and K are 1.68 and 0.428, and for just r, 0.267. For NH_4Cl, 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, Vazquez 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.

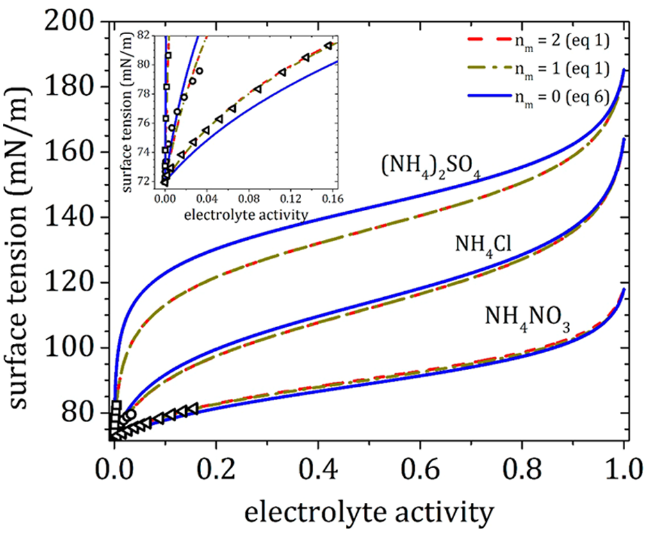


Figure 4. Surface tension as a function of electrolyte activity for ammonium sulfate, ammonium chloride, and ammonium nitrate. For all curves, pure solute surface tension (σ_S) predictions were obtained from ref 16. The red dashed line is eq 1, using parameters r and K. The dark yellow dash-dot line 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.

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.[18−20] 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 σ_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 σ_s. Since σ_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 v 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, σ_S, from Dutcher et al.[16] 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_p 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.

DOI: 10.1021/acs.jpclett.5b01346
J. Phys. Chem. Lett. 2015, 6, 3384−3389

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[28] and surface forces produced by image charges and ion hydration,[29] as well as in crucial applications ranging from desalination of water[30] to atmospheric aerosol particle dynamics modeling.[31,32]

■ ASSOCIATED CONTENT

Ⓢ 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.jpclett.5b01346.

(PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cdutcher@umn.edu.

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.

■ ACKNOWLEDGMENTS

H.B. was supported through a National Science Foundation Graduate Research Fellowship. Part of this work was carried out in the College of Science and Engineering Coating Process and Visualization Laboratory, University of Minnesota, which has received capital equipment funding from the NSF through the UMN MRSEC under Award DMR-1420013.

■ REFERENCES

(1) Coury, C.; Dillner, A. M. A Method to Quantify Organic Functional Groups and Inorganic Compounds in Ambient Aerosols Using Attenuated Total Reflectance FTIR Spectroscopy and Multivariate Chemometric Techniques. *Atmos. Environ.* **2008**, *42*, 5923−5932.

(2) Maria, S. F.; Russell, L. M.; Turpin, B. J.; Porcja, R. J. FTIR Measurements of Functional Groups and Organic Mass in Aerosol Samples Over the Caribbean. *Atmos. Environ.* **2002**, *36*, 5185−5196.

(3) Maria, S. F.; Russell, L. M.; Gilles, M. K.; Myneni, S. C. B. Organic Aerosol Growth Mechanisms and Their Climate-Forcing Implications. *Science* **2004**, *306*, 1921−1924.

(4) Aiken, A. C.; Decarlo, P. F.; Kroll, J. H.; Worsnop, D. R.; Huffman, J. A.; Docherty, K. S.; Ulbrich, I. M.; Mohr, C.; Kimmel, J. R.; et al. O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry. *Environ. Sci. Technol.* **2008**, *42*, 4478−4485.

(5) Saunders, S. M.; Jenkin, M. E.; Derwent, R. G.; Pilling, M. J. Protocol for the Development of the Master Chemical Mechanism, MCM vs3 (Part A): Tropospheric Degradation of Non-Aromatic Volatile Organic Compounds. *Atmos. Chem. Phys.* **2003**, *3*, 161−180.

(6) Valorso, R.; Aumont, B.; Camredon, M.; Raventos-Duran, T.; Mouchel-Vallon, C.; Ng, N. L.; Seinfeld, J. H.; Lee-Taylor, J.; Madronich, S. Explicit Modelling of SOA Formation from α-pinene Photooxidation: Sensitivity to Vapour Pressure Estimation. *Atmos. Chem. Phys.* **2011**, *11*, 6895−6910.

(7) Robinson, A. L.; Donahue, N. M.; Shrivastava, M. K.; Weitkamp, E. A.; Sage, A. M.; Grieshop, A. P.; Lane, T. E.; Pierce, J. R.; Pandis, S. N. Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging. *Science* **2007**, *315*, 1259−1262.

(8) Cappa, C. D.; Wilson, K. R. Multi-Generation Gas-Phase Oxidation, Equilibrium Partitioning and the Formation and Evolution of Secondary Organic Aerosol. *Atmos. Chem. Phys.* **2012**, *12*, 9505−9528.

(9) Hu, J.; Zhang, X.; Wang, Z. A Review on Progress in QSPR Studies for Surfactants. *Int. J. Mol. Sci.* **2010**, *11*, 1020−1047.

(10) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Structure-Activity Analysis*; Research Studies Press: Letchworth, England, 1986; Vol. *9*.

(11) Stankevich, M. I.; Stankevich, I. V.; Zefirov, N. S. Topological Indices in Organic Chemistry. *Russ. Chem. Rev.* **1988**, *57*, 191−208.

(12) Stewart, J. J. P. *MOPAC 6.0: A General Purpose Molecular Orbital Package*; Frank J. Seiler Research Laboratory, U.S. Air Force Academy: Colorado Springs, CO, 1989.

(13) Wexler, A. S.; Dutcher, C. S. Statistical Mechanics of Multilayer Sorption: Surface Tension. *J. Phys. Chem. Lett.* **2013**, *4*, 1723−1726.

(14) Wang, P.; Anderko, A.; Young, R. D. Modeling Surface Tension of Concentrated and Mixed-Solvent Electrolyte Systems. *Ind. Eng. Chem. Res.* **2011**, *50*, 4086−4098.

(15) Pegram, L.; Record, M. T., Jr. Hofmeister Salt Effects on Surface Tension Arise from Partitioning of Anions and Cations Between Bulk Water and the Air-Water Interface. *J. Phys. Chem. B* **2007**, *111*, 5411−5417.

(16) Dutcher, C. S.; Wexler, A. S.; Clegg, S. L. Surface Tensions of Inorganic Multicomponent Aqueous Electrolyte Solutions and Melts. *J. Phys. Chem. A* **2010**, *114*, 12216−12230.

(17) Szyszkowski, v. B. Experimentelle Studien uber kapillare Eigenschaften der wassrigen Losungen von Fettsauren. *Z. Phys. Chem.* **1908**, *64*, 385.

(18) Dutcher, C. S.; Ge, X.; Wexler, A. S.; Clegg, S. L. Statistical Mechanics of Multilayer Sorption: Extension of the Brunauer-Emmett-Teller (BET) and Guggenheim-Anderson-deBoer (GAB) Adsorption Isotherms. *J. Phys. Chem. C* **2011**, *115*, 16474−16487.

(19) Dutcher, C. S.; Ge, X.; Wexler, A. S.; Clegg, S. L. Statistical Mechanics of Multilayer Sorption. 2. Systems Containing Multiple Solutes. *J. Phys. Chem. C* **2012**, *116*, 1850−1864.

(20) Dutcher, C. S.; Ge, X.; Wexler, A. S.; Clegg, S. L. An Isotherm-Based Thermodynamic Model of Aqueous Solutions, Applicable Over the Entire Concentration Range. *J. Phys. Chem. A* **2013**, *117*, 3198−3213.

(21) Brunauer, S.; Emmett, P. H.; Teller, E. J. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, *60*, 309−319.

(22) Guggenheim, E. A. *Applications of Statistical Mechanics*; Clarendon Press: Oxford, U.K., 1966.

(23) Anderson, R. B. Modifications of the Brunauer, Emmett and Teller Equation. *J. Am. Chem. Soc.* **1946**, *68*, 686−691.

(24) de Boer, J. H. *The Dynamical Character of Adsorption*; Clarendon Press: Oxford, U.K., 1968.

(25) Ally, M. R.; Braunstein, J. Statistical Mechanics of Multilayer Adsorption: Electrolyte and Water Activities in Concentrated Solutions. *J. Chem. Thermodyn.* **1998**, *30*, 49−58.

(26) Vazquez, G.; Alvarez, E.; Navaza, J. M. Surface Tension of Alcohol + Water from 20 to 50 deg C. *J. Chem. Eng. Data* **1995**, *40*, 611−614.

(27) Washburn, E.; West, C. J.; Hull, C. *International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*; Cornell University: Ithaca, NY, 1928; Vol. *4*.

(28) Drzymala, J.; Lyklema, J. Surface Tension of Aqueous Electrolyte Solutions. Thermodynamics. *J. Phys. Chem. A* **2012**, *116*, 6465−6472.

(29) Slavchov, R. I.; Novev, J. K. Surface Tension of Concentrated Electrolyte Solutions. *J. Colloid Interface Sci.* **2012**, *387*, 234−243.

(30) Nayar, K. G.; Panchanathan, D.; McKinley, G. H.; Lienhard, J. H. V. Surface Tension of Seawater. *J. Phys. Chem. Ref. Data* **2014**, *43*, 043103.

(31) Schwier, A. N.; Viglione, G. A.; Li, Z.; McNeill, V. F. Modeling the Surface Tension of Complex, Reactive Organic-Inorganic Mixtures. *Atmos. Chem. Phys.* **2013**, *13*, 10721−10732.

(32) McNeill, V. F.; Sareen, N.; Schwier, A. N. Surface-Active Organics in Atmospheric Aerosols. *Top. Curr. Chem.* **2014**, *339*, 201−259.

(33) Nakanishi, K.; Matsumoto, T.; Hayatsu, M. Surface Tension of Aqueous Solutions of Some Glycols. *J. Chem. Eng. Data* **1971**, *16*, 44−45.

(34) Yamada, M.; Fukusako, S.; Kawanami, T.; Sawada, I.; Horibe, A. Surface Tension of Aqueous Binary Solutions. *Int. J. Thermophys.* **1997**, *18*, 1483−1493.

(35) Ernst, R. C.; Watkins, C. H.; Ruwe, H. H. The Physical Properties of The Ternary System Ethyl Alcohol-Glycerin-Water. *J. Phys. Chem.* **1936**, *40*, 627−635.

(36) Ohm, P.; Asato, C.; Wexler, A. S.; Dutcher, C. S. Isotherm-Based Thermodynamic Model for Electrolyte and Nonelectrolyte Solutions Incorporating Long- and Short-Range Electrostatic Interactions. *J. Phys. Chem. A* **2015**, *119*, 3244−3252.

(37) Abramzon, A. A.; Gaukhberg, R. D. Surface Tension of Salt Solutions. *Russ. J. Appl. Chem.* **1993**, *Vol. 66* (No. 7 Part 2), 1315−1320.

(38) Abramzon, A. A.; Gaukhberg, R. D. Surface Tension of Salt Solutions. *Russ. J. Appl. Chem.* **1993**, *66* (No. 8, Part 2), 1473−1479.