

# UC Davis

## UC Davis Previously Published Works

### Title

Statistical Mechanics of Multilayer Sorption: Surface Concentration Modeling and XPS Measurement

### Permalink

<https://escholarship.org/uc/item/0cq4k5gs>

### Journal

The Journal of Physical Chemistry Letters, 9(6)

### ISSN

1948-7185

### Authors

Toribio, Anthony R  
Prisle, Nønne L  
Wexler, Anthony S

### Publication Date

2018-03-15

### DOI

10.1021/acs.jpcllett.8b00332

Peer reviewed

# Statistical Mechanics of Multilayer Sorption: Surface Concentration Modeling and XPS Measurement

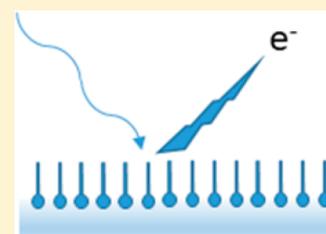
Anthony R. Toribio,<sup>†</sup> Nønne L. Prisle,<sup>‡</sup> and Anthony S. Wexler<sup>\*,†,§</sup>

<sup>†</sup>Mechanical and Aerospace Engineering, University of California, Davis, California 95616, United States

<sup>‡</sup>Synchrotron-based Atmospheric Research, Nano and Molecular Systems Research Unit, University of Oulu, PO Box 3000, Oulu 90014, Finland

<sup>§</sup>Civil and Environmental Engineering, Land, Air and Water Resources and Air Quality Research Center, University of California, Davis, California 95616, United States

**ABSTRACT:** The concentration of solute molecules at the surface of a liquid is a factor in heterogeneous reactions, surface tension, and Marangoni-effect-driven surface flows. Increasingly, X-ray photoelectron spectroscopy (XPS) has enabled surface concentrations to be measured. In prior work, we employed statistical mechanics to derive expressions for surface tension as a function of solute activity in a binary solution. Here we use a Gibbs relation to derive concomitant expressions for surface concentration. Surface tension data from the literature for five alcohols are used to identify parameters in the surface tension equation. These parameters are then used in the surface concentration equation to predict surface concentrations. Comparison of these predictions to those measured with XPS shows a factor of three difference between measured and predicted surface concentrations. Potential reasons for the discrepancy are discussed, including lack of surface-bulk equilibrium in the measurements.



As Wolfgang Pauli stated, “God made the bulk; surfaces were invented by the devil.” Yet modern technology, science, and engineering continue to appreciate and exploit the importance of surfaces because feature size in microelectronics becomes smaller, nucleation of atmospheric aerosol particles influences climate, and the complexity of protein folding in cell bilayers governs numerous biological processes. Over the past decade, Dutcher, Clegg, Wexler, and coworkers have used the statistical mechanics of multilayer sorption to describe thermodynamics of the bulk<sup>1–7</sup> and the surface<sup>8–10</sup> in complex and highly concentrated mixtures and related the parameter values in these equations to physicochemical properties of the solvent and solute. In parallel, experimental methods for measuring the concentration of solutes at the surface of solutions continue to improve.

A breakthrough for liquid systems was made with the invention of the liquid microjet,<sup>11</sup> enabling the use of surface-sensitive XPS (X-ray photoelectron spectroscopy) for systems of high vapor pressure and the successful use of the technique for aqueous organics of immediate relevance for atmospheric aerosols and cloud droplets.<sup>12,13</sup> Recently, liquid jet XPS was used to measure the surface concentration of alcohols in an aqueous solution.<sup>14,15</sup> In this work, we use the binary surface tension equation of Wexler and Dutcher,<sup>8</sup> along with a Gibbs relation to derive expressions for surface concentration. Then, we use surface tension data to identify the surface parameters in the surface tension equation. Finally, we use these parameter values in the surface concentration equation to predict such concentrations and compare to XPS measurements to obtain insights into the meaning and predictability of surface concentration.

Using a Gibbs relation, expressions for the surface excess concentration can be derived from expressions for surface tension. The Gibbs relation for surface excess concentration is

$$\Gamma_A^x(a_A) = -\frac{a_A}{kT} \frac{d\sigma(a_A)}{da_A} \quad (1)$$

where  $a_A$  is the activity of the solute in solution, the superscript  $x$  indicates surface excess,  $kT$  is Boltzmann’s constant multiplied by temperature, and  $\sigma$  is the surface tension. Wexler and Dutcher<sup>8</sup> used statistical mechanics to derive expressions for surface tension as a function of solute activity. They assumed that surface-active solute molecules displace water molecules from the surface. The random distribution of the remaining water molecules and solute molecules on the surface leads to the entropy of the surface system. The resulting general equation is

$$\sigma = \sigma_W + \frac{kT}{rS_W} \ln \left( \frac{1 - Ka_A}{1 - Ka_A(1 - C)} \right) \quad (2)$$

which corresponds to equation 9 of Wexler and Dutcher,<sup>8</sup> where  $r$  is generally the number of water molecules displaced from the surface by each solute molecule,  $S_W$  is the surface area occupied by one water molecule,  $\sigma_W = 72$  mN/m is the surface tension of pure water,  $kT/S_W = 41$  mN/m for water as the solvent at 298 K, and  $K$  and  $C$  are parameters related to the energy of the solute in the bulk and at the surface.

**Received:** January 31, 2018

**Accepted:** March 6, 2018

**Published:** March 7, 2018

A couple of special cases arise from limits of the parameter values in eq 2, which correspond to equation 9 in Wexler and Dutcher.<sup>8</sup> For instance, the limits for highly surface-active solutes such as alcohols lead to the von Szyszkowski equation<sup>16</sup> (equation 10 of Wexler and Dutcher<sup>8</sup>). Using eq 2 here and special cases of it given by equations 10 and 11 of Wexler and Dutcher<sup>8</sup> with eq 1 gives corresponding equations for surface excess concentration

$$\Gamma_A^x(a_A) = \frac{CKa_A}{rS_W(1 - Ka_A)(1 - Ka_A(1 - C))} \quad (3)$$

where the subscript W indicates solvent, water in this case.

$$\Gamma_A^x(a_A) = \frac{Ka_A}{rS_W(1 + Ka_A)} \quad (4)$$

$$\Gamma_A^x(a_A) = \frac{CKa_A}{rS_W(1 - Ka_A)^2} \quad (5)$$

Equation 3 is the “full” equation for surface excess concentration of a solute, corresponding to eq 2 here. Equation 4 is a simplified form that generally applies for highly soluble compounds with high surface affinity, such as alcohols, and is derived from equation 10 of Wexler and Dutcher,<sup>8</sup> which is a form of the von Szyszkowski equation.<sup>16</sup> Equation 5 is a simplified form of eq 3 that generally applies to electrolytes. See Wexler and Dutcher<sup>8</sup> (2013) for more details of the limits where their equations 9–11 apply and therefore where eqs 3–5 here apply and for the meaning of the parameters in these equations.

The objective of this work is to predict surface excess concentration from eq 3 using surface tension data in eq 2 to identify the unknown parameters. For all solutes, the procedure is

1. Obtain surface tension data from the literature.
2. Fit these data to eq 2, identifying the values of  $r$ ,  $K$ , and  $C$ .
3. Use these values of  $r$ ,  $K$ , and  $C$  in eq 3 to predict surface excess concentration.
4. Compare these predicted concentrations to those measured by Walz and colleagues<sup>14,15</sup> for 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and *t*-butanol.

Surface pressure data for the *n*-alkanols were obtained from Posner and colleagues<sup>17</sup> and were converted to surface tension by subtracting from the surface tension of pure water. The surface tension for *tert*-butanol was obtained from Hey and Kippax.<sup>18</sup> Because these data were from dilute solutions, the activity coefficient was assumed to be sufficiently close to one so that activity was assumed to be well approximated by the mole fraction. Table 1 lists the values obtained by fitting eq 2 to these surface tension data using the Solver feature of Microsoft Excel to minimize the total squared error between the equation and the data.

The fits for eq 3 to the surface tension are very good, as indicated by the mean absolute error in Table 1. Figures 1–5 show the surface concentration data of Walz and colleagues (dots) and the surface concentration predicted from eq 3 using the values in Table 1 (dashed lines). In all cases the predictions are higher than the measurements, as seen from the respective values of fitted parameter  $r$  in Table 1. The surface concentration data were fit to eq 3, letting the value of  $r$  vary while keeping the values of  $K$  and  $C$  the same. The second to last column of Table 1 lists the fit  $r$  values, while the last

Table 1. Parameter Values and Goodness of Fit for Equation 3

solute	fit to surface tension data			fit to surface concentration data		
	$r$	$K$	$C$	mean absolute error (%)	$r$	mean absolute error (%)
1-butanol	1.11	1.00	867	0.73	2.4	16
1-pentanol	1.01	0.26	13 000	1.1	2.7	5
1-hexanol	0.85	0.84	9278	1.1	2.8	7
1-heptanol	0.88	1.11	26 882	1.0	2.9	1
<i>t</i> -butanol	2.93	0.18	51 759	4.3	4.7	18

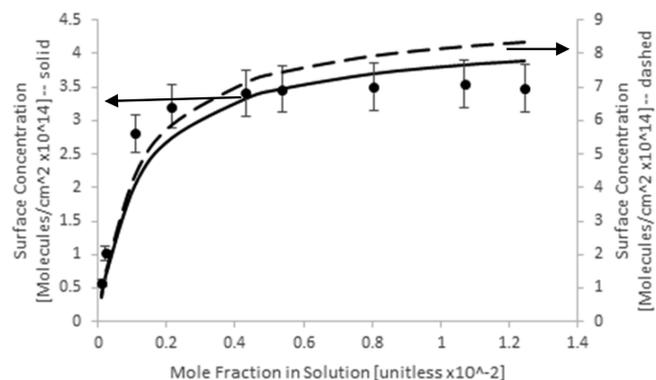


Figure 1. Surface concentration of aqueous 1-butanol. Dots: measurements; solid line: fit of eq 3 through the data only varying the value of  $r$ ; dashed line: eq 3 predictions. Measurements and solid line fit use the left vertical axis. Dashed line prediction used the right vertical axis.

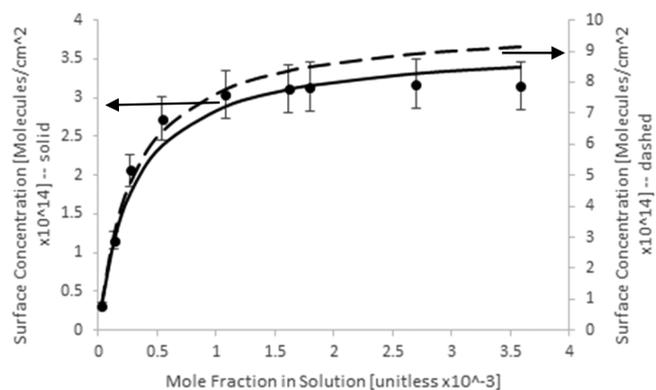
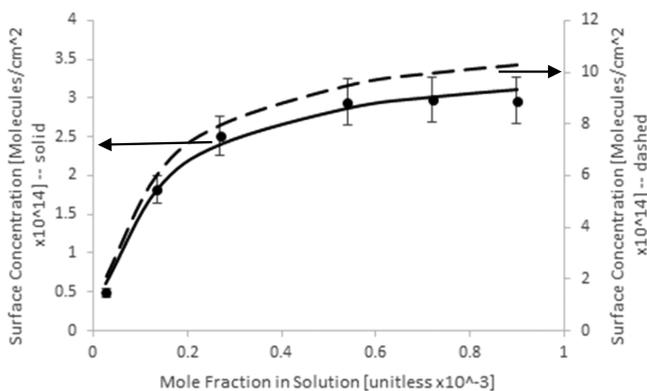


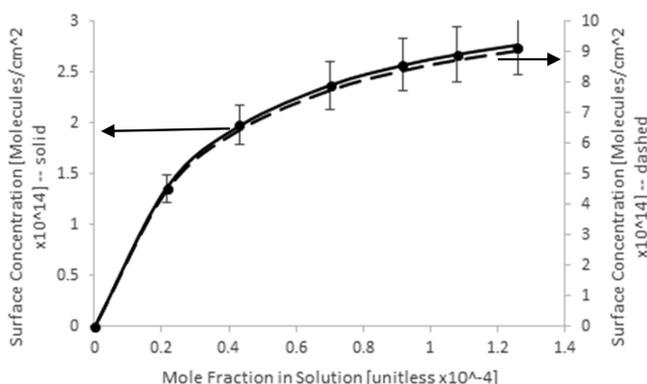
Figure 2. Surface concentration of aqueous 1-pentanol. See legend of Figure 1 for description.

column lists the resulting mean absolute error. Note that the mean absolute error for *t*-butanol is large due to large relative error for the two smallest concentration values.

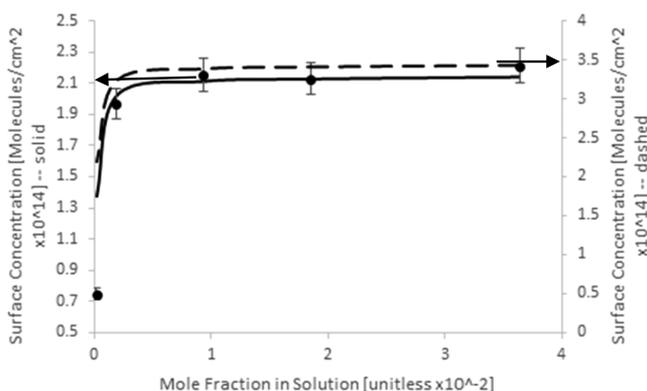
Equations 3–5 provide the Gibbs excess surface concentration, which is not necessarily equal to the physical surface concentration of the solute. Equation 6 relates the surface excess concentration to the physical surface concentrations of the solute,  $\Gamma_A$ , and solvent,  $\Gamma_W$ , in terms of the number of molecules of each,  $N_A$  and  $N_W$ , in the bulk.<sup>19</sup> The surface excess and physical surface concentrations are equivalent, though, for either dilute solution because  $N_A/N_W$  is small, or for highly surface active compounds, such as long-chain alcohols, because for even modest bulk solute concentrations  $\Gamma_W$  is small. Both conditions apply here.



**Figure 3.** Surface concentration of aqueous 1-hexanol. See legend of Figure 1 for description.



**Figure 4.** Surface concentration of aqueous 1-heptanol. See legend of Figure 1 for description.



**Figure 5.** Surface concentration of aqueous *t*-butanol. See legend of Figure 1 for description.

$$\Gamma_A^x = \Gamma_A - \Gamma_W \frac{N_A}{N_W} \quad (6)$$

Although the surface concentration predictions are higher than those observations, the shapes of the curves are very similar. They rise at about the same rate and then level out at about the same solute mole fraction.

There are a number of possible explanations for the discrepancy between the predicted and measured surface concentrations. First, surface concentration is notoriously difficult to model and measure for a number of reasons, one of which is that the surface layer can be defined in a number or thermodynamically consistent ways.<sup>20</sup> Second, the surface

tension data may be flawed, but both sources of surface tension data<sup>17,18</sup> employed here measured the surface tension of *n*-pentanol and obtained almost exactly the same values, so the surface tension data seem reliable.

Third, we consider the surface concentration data itself. A number of assumptions are involved in converting XPS spectra to surface concentrations.<sup>21</sup> Two aspects, in particular, may influence the ability to derive quantitative information from XPS: (A) The surface may not have been in equilibrium with the bulk for two reasons: Walz et al. (2015, 2016) report measurements on a microjet traveling at 26.5 m/s, performed  $\sim 1$  mm from the nozzle. This means the surface age is  $\sim 0.00004$  s at the time of measurement. The interaction time of the X-rays with the sample is much shorter than this. The jet has a diameter of 20  $\mu\text{m}$ , so with diffusion coefficients of, for example,  $1.28 \times 10^{-5}$ ,  $1 \times 10^{-5}$ ,  $0.87 \times 10^{-5}$ , and  $0.77 \times 10^{-5}$   $\text{cm}^2/\text{s}$  for methanol, ethanol, 1-propanol, and 1-butanol, respectively, surfaces would need time scales of 0.01 s or more to equilibrate. Diffusion is slower for the larger alcohols, which would bias surface concentrations low compared with smaller alcohols, which is in line with the increased difference between model and XPS concentrations with increasing chain length for the normal alcohols. The jet travels into vacuum where both water and alcohol will evaporate from the jet surface. Walz et al. scale the maximum surface XPS signal relative to pure liquid alcohol to quantify surface concentrations. Insufficient diffusion time and possible evaporation therefore cannot in itself explain the difference between modeled and XPS-derived surface concentrations. (B) XPS measurements may be so surface-sensitive that concentrations obtained from simply integrating C 1s peak areas may be underestimated for larger, more surface active alcohols, especially at higher concentrations. In the papers by Walz et al., the C 1s signal from hydroxyl carbons is increasingly suppressed with respect to the aliphatic carbons, indicating that the former is disproportionately attenuated as alcohol molecules arrange in an increasingly “upright” position perpendicular to the water surface. The effective attenuation length (EAL) of photoelectrons is estimated to  $\sim 1$  nm. The signal decays exponentially with distance into the sample, and 95% of the signal arrives from a depth less than  $3 \times \text{EAL}$ , and the suppression of the hydroxyl C 1s means that over a distance shorter than the length of one molecule, the signal is already significantly attenuated. This will lead to an increasing underestimation of surface concentrations for the longer and more upright oriented alcohol chains. It is also increasingly likely that subsurface layers are significantly enriched for the more surface-active alcohols, such that the attenuation of signal from subsurface layers leads to increasing underestimation of the total concentration of alcohol in the surface region.

At this point, it is not possible to quantify the bias in individual cases, and the viability of XPS to obtain realistic information on surface concentrations and surface tension for larger surface-active molecules, in a manner similar to that of Werner and coworkers,<sup>22</sup> needs to be carefully examined in future work. Here we simply note the similarities in trends between modeled and XPS-derived surface concentrations.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [aswexler@ucdavis.edu](mailto:aswexler@ucdavis.edu).

ORCID 

Anthony S. Wexler: 0000-0003-1565-814X

## Notes

The authors declare no competing financial interest.

## ■ REFERENCES

- (1) 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–de Boer (GAB) adsorption isotherms. *J. Phys. Chem. C* **2011**, *115* (33), 16474–16487.
- (2) 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* (2), 1850–1864.
- (3) Dutcher, C. S.; Ge, X.; Wexler, A. S.; Clegg, S. L. An isotherm-based thermodynamic model of multicomponent aqueous solutions, applicable over the entire concentration range. *J. Phys. Chem. A* **2013**, *117* (15), 3198–3213.
- (4) Ohm, P. B.; 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* (13), 3244–3252.
- (5) Nandy, L.; Ohm, P. B.; Dutcher, C. S. Isotherm-Based Thermodynamic Models for Solute Activities of Organic Acids with Consideration of Partial Dissociation. *J. Phys. Chem. A* **2016**, *120* (24), 4147–4154.
- (6) Nandy, L.; Dutcher, C. S. Isotherm-Based Thermodynamic Model for Solute Activities of Asymmetric Electrolyte Aqueous Solutions. *J. Phys. Chem. A* **2017**, *121*, 6957.
- (7) Marsh, A.; Miles, R. E.; Rovelli, G.; Cowling, A. G.; Nandy, L.; Dutcher, C. S.; Reid, J. P. Influence of organic compound functionality on aerosol hygroscopicity: dicarboxylic acids, alkyl-substituents, sugars and amino acids. *Atmos. Chem. Phys.* **2017**, *17* (9), 5583–5599.
- (8) Wexler, A. S.; Dutcher, C. S. Statistical mechanics of multilayer sorption: Surface tension. *J. Phys. Chem. Lett.* **2013**, *4* (10), 1723–1726.
- (9) Boyer, H.; Wexler, A.; Dutcher, C. S. Parameter interpretation and reduction for a unified statistical mechanical surface tension model. *J. Phys. Chem. Lett.* **2015**, *6* (17), 3384–3389.
- (10) Boyer, H. C.; Dutcher, C. S. Statistical Thermodynamic Model for Surface Tension of Aqueous Organic Acids with Consideration of Partial Dissociation. *J. Phys. Chem. A* **2016**, *120* (25), 4368–4375.
- (11) Winter, B.; Faubel, M. Photoemission from liquid aqueous solutions. *Chem. Rev.* **2006**, *106* (4), 1176–1211.
- (12) Prisle, N.; Ottosson, N.; Öhrwall, G.; Söderström, J.; Dal Maso, M.; Björneholm, O. Surface/bulk partitioning and acid/base speciation of aqueous decanoate: direct observations and atmospheric implications. *Atmos. Chem. Phys.* **2012**, *12* (24), 12227–12242.
- (13) Werner, J. *Exploring the Surface of Aqueous Solutions: X-ray Photoelectron Spectroscopy Studies Using a Liquid Micro-Jet*. Ph.D. Thesis, Acta Universitatis Upsaliensis, 2015.
- (14) Walz, M.-M.; Caleman, C.; Werner, J.; Ekholm, V.; Lundberg, D.; Prisle, N.; Öhrwall, G.; Björneholm, O. Surface behavior of amphiphiles in aqueous solution: a comparison between different pentanol isomers. *Phys. Chem. Chem. Phys.* **2015**, *17* (21), 14036–14044.
- (15) Walz, M.-M.; Werner, J.; Ekholm, V.; Prisle, N.; Öhrwall, G.; Björneholm, O. Alcohols at the aqueous surface: chain length and isomer effects. *Phys. Chem. Chem. Phys.* **2016**, *18* (9), 6648–6656.
- (16) Szyszkowski, B. v. Experimentelle Studien über kapillare Eigenschaften der wässrigen Lösungen von Fettsäuren. *Z. Phys. Chem.* **1908**, *64* (1), 385–414.
- (17) Posner, A.; Anderson, J.; Alexander, A. The surface tension and surface potential of aqueous solutions of normal aliphatic alcohols. *J. Colloid Sci.* **1952**, *7* (6), 623–644.
- (18) Hey, M.; Kippax, P. Surface tensions of mixed aqueous solutions of tert-butanol and n-pentanol. *Colloids Surf., A* **2005**, *262* (1), 198–203.
- (19) Bermúdez-Salguero, C.; Gracia-Fadrique, J. s. Gibbs excess and the calculation of the absolute surface composition of liquid binary mixtures. *J. Phys. Chem. B* **2015**, *119* (17), 5598–5608.
- (20) Guggenheim, E.; Adam, N. The thermodynamics of adsorption at the surface of solutions. *Proc. R. Soc. London, Ser. A* **1933**, *139* (837), 218–236.
- (21) Seidel, R.; Winter, B.; Bradforth, S. E. Valence electronic structure of aqueous solutions: Insights from photoelectron spectroscopy. *Annu. Rev. Phys. Chem.* **2016**, *67*, 283–305.
- (22) Werner, J.; Julin, J.; Dalirian, M.; Prisle, N. L.; Öhrwall, G.; Persson, I.; Björneholm, O.; Riipinen, I. Succinic acid in aqueous solution: connecting microscopic surface composition and macroscopic surface tension. *Phys. Chem. Chem. Phys.* **2014**, *16* (39), 21486–21495.