Supporting Material to:

Chemical Composition and Properties of the Liquid – Vapor Interface of Aqueous C1 to C4 Monofunctional Acid and Alcohol Solutions

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Supporting information

This supporting material contains additional spectroscopy information, a table with solution pH and carbon 1s photoemission intensity, and a description of how the surface excess was derived from surface tension measurements.

Additional spectroscopy information

The O 1s XP regions from a liquid microjet of 0.5 M aqueous organics-water solutions are shown in Fig. S1. The O 1s region is fit by two components that are assigned to gas phase oxygen (mainly $H_2O_{(g)}$) at higher BE and condensed phase oxygen ($H_2O_{(liq)}$), $RCH_xO_{y(aq)}$) at lower BE. Because the O 1s levels attributed to oxygen of condensed phase alcohol and carboxyl groups strongly overlap with that of H_2O, we refrain from fitting detailed components to the condensed phase O 1s peak.
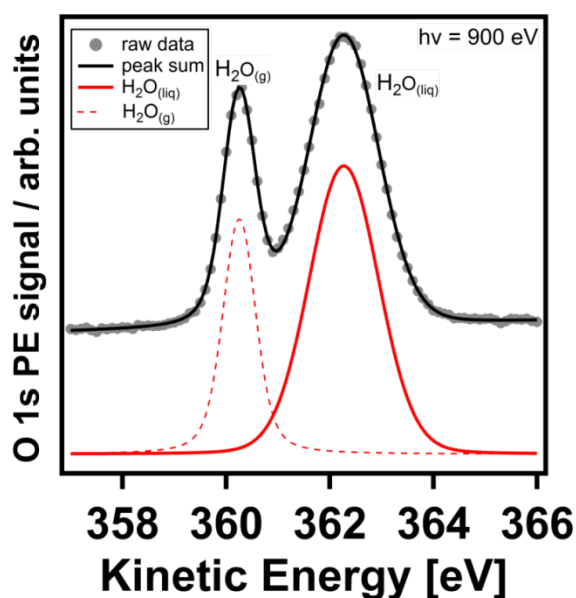

Figure S1. O 1s photoemission spectrum from a 0.5 M formic acid aqueous solution excited by 900 eV photons. The spectrum exhibits two components that are assigned as O 1s(gas) and O 1s(liq).

Table S1. pH of solutions investigated and relative intensity of the functional group carbon 1s photoemission signal

Organic Solute	pH	C 1s intensity*
Formate, $HCOO^-$	12.8	0.07
Acetate, CH_3-COO^-	12.9	0.1
Propanoate, CH_3CH_2-COO^-	12.8	0.12
Butyrate, $CH_3CH_2CH_2$-COO^-	12.6	0.19
Methanol, CH_3-OH	-	0.22
Formic acid, HCOOH	2.2	0.34
Ethanol, CH_3CH_2-OH	-	0.46
Acetic acid, CH_3-COOH	2.6	0.55
2-Propanol, CH_3CH-OH-CH_3	-	0.71
Propanoic Acid, CH_3CH_2-COOH	2.7	0.72
1-Propanol, $CH_3CH_2CH_2$-OH	-	0.74
Butyric Acid, $CH_3CH_2CH_2$ COOH	2.7	0.86
1-Butanol, $CH_3CH_2CH_2CH_2$-OH	-	1

* all values are normalized to the functional group carbon 1s of 1-butanol

Calculation of surface excess

In the thermodynamic development of surface tension, it is directly related by the Gibbs equation to the surface excess (n_{se}), Γ_i, of a component i beyond a theoretical dividing plane (referred to as the Gibbs surface) placed parallel to the solution surface[1]

$$\Gamma_i = -\frac{X_i}{RT}\left(\frac{\partial\gamma}{\partial X_i}\right)_T \qquad (S1)$$

where X_i is the mole fraction of component i, R is the universal gas constant and T is temperature in Kelvin. In solutions containing multiple species, different molecular arrangements can give rise to similar measures of surface tension, complicating direct interpretation of the results. The temperature range was between 293 and 300 K. The majority of surface tension values were taken at 298K.

Fig. S2 depicts exemplary surface tension data. To determine the surface excess of butyric acid at the interface the semi-empirical Meissner-Michaels equation was used to fit the surface tension data:[2,3]

$$\gamma = \gamma_0\left[1 - b\ln(\frac{X_i}{a}+1)\right] \qquad (S2)$$

where γ_0 is the surface tension of pure water, and *a* and *b* are fitting parameters, which are provided in the inset of Fig. S2 for the example of butyric acid as fit to the data of Granados et al. (2006).[4]

$$\gamma = \gamma_0\left[1 - b\ln\left(\frac{C_i}{a} + 1\right)\right]$$

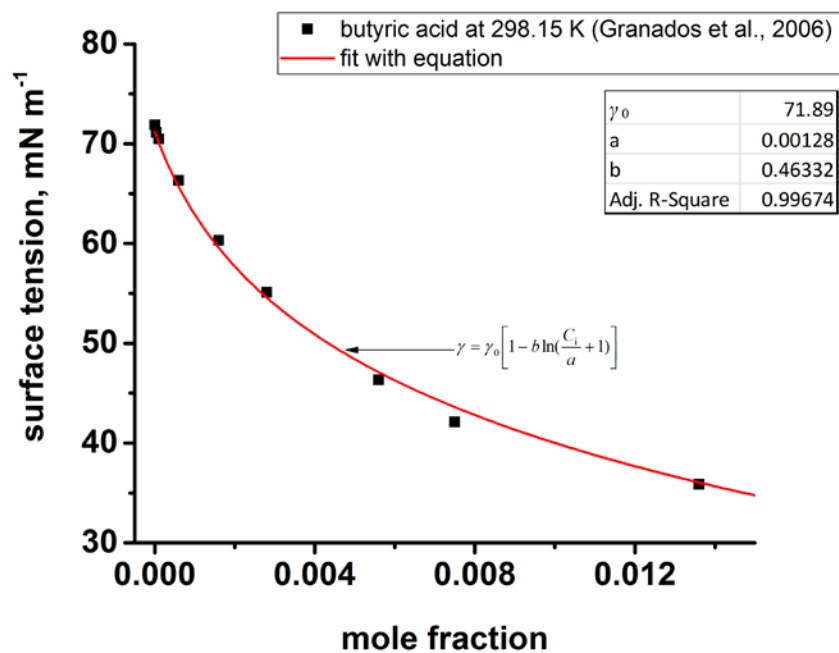|	
γ_0	71.89
a	0.00128
b	0.46332
Adj. R-Square	0.99674

Figure S2. Exemplary surface tension is plotted as a function of butyric acid mole fraction. The measured data are shown with marker. The line displays the best fit of the data to the Meissner-Michael equation (S2). The values *a* and *b* are fitting parameters given in equation (S2).

Figures S3, S4 and S5 show the results from taking the first derivative of the surface tension as a function of the butyric acid and 1-butanol concentration respectively, as fit to the Meissner-Michael equation, and using equation (S1) to calculate the surface excess Γ.
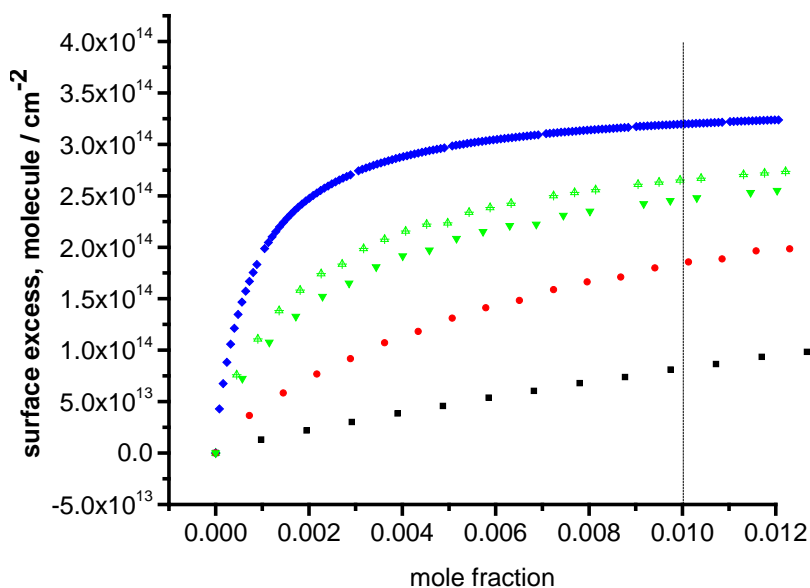
Figure S3. Surface excesses of methanol (black squares), ethanol (red crosses), 1-propanol (green upward triangles), 2-propanol (green downward triangles) and butanol (blue diamonds) derived using the Gibbs equation and the experimental data from surface tension measurements. The dashed line indicates the 0.01 mole fraction corresponding to 0.5 M used in most of the XPS measurements.
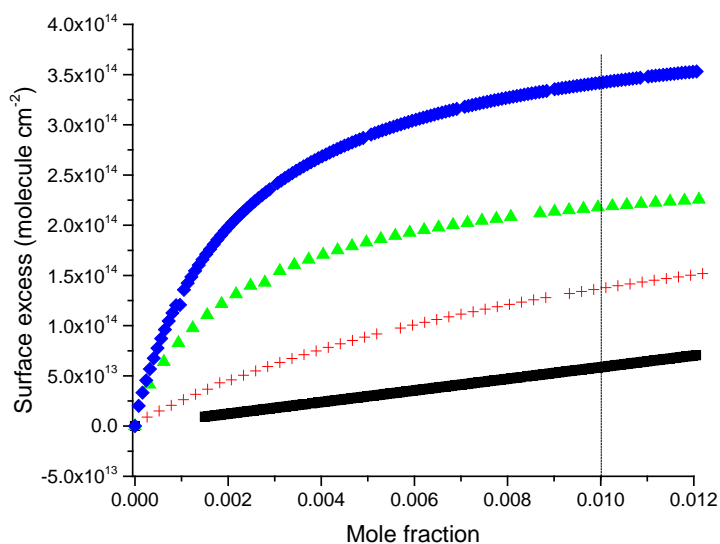

Figure S4. Surface excesses of formic acid (black squares), acetic acid (red crosses), propanoic acid (green triangles) and butyric acid (blue diamonds) solutions derived using the Gibbs

equation and the experimental data from surface tension measurements. The dashed line

indicates the 0.01 mole fraction corresponding to 0.5 M used in most of the XPS measurements.
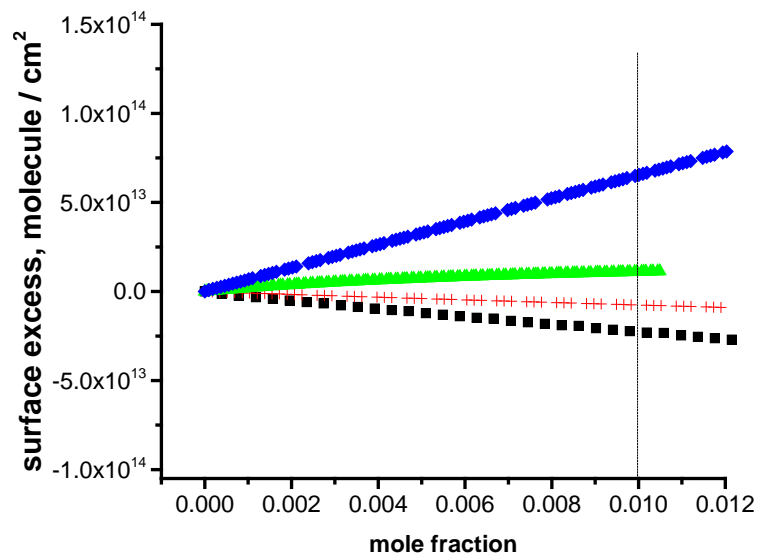

Figure S5. Surface excesses of sodium formate (black squares), acetate (red crosses), propanoate (green triangles) and butyrate (blue diamonds) solutions derived using the Gibbs equation and the experimental data from surface tension measurements. The dashed line indicates the 0.01 mole fraction corresponding to 0.5 M used in most of the XPS measurements.

References

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2. Langmuir, I., The Constitution and Fundamental Properties of Solids and Liquids. II Liquids. *J. Am. Chem. Soc.* **1917**, *39*, 1848-1906.

3. Meissner, H. P.; Michaels, A. S., Surface Tension of pure Liquids and Liquid Mixtures. *Ind. Eng. Chem*. **1949**, *41*, 2782-2787.

4. Granados, K.; Gracia-Fadrique, J.; Amigo, A.; Bravo, R., Refractive Index, Surface Tension, and Density of Aqueous Mixtures of Carboxylic Acids at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 1356-1360.