Electronic supplementary information for:

Succinic acid in aqueous solution: Connecting microscopic surface composition and macroscopic surface tension

Josephina Werner[a,b], Jan Julin[c], Maryam Dalirian[c], Nønne L. Prisle[d], Gunnar Öhrwall[e], Ingmar Persson[b], Olle Björneholm[a], and Ilona Riipinen[c,f]

[a] *Department of Physics and Astronomy, Uppsala University, P.O. Box 516, SE-751 20 Uppsala, Sweden Tel: +4618 471 3561; E-mail: josephina.werner@physics.uu.se*

[b] *Department of Chemistry and Biotechnology, Swedish University of Agricultural Sciences, P.O. Box 7015, SE-750 07 Uppsala, Sweden*

[c] *Department of Applied Environmental Science and Bolin Centre for Climate Research, Stockholm University, SE-106 91 Stockholm, Sweden*

[d] *Department of Physics, Helsinki University, P.O. Box 48, F-00014 Helsinki, Finland*

[e] *MAX IV Laboratory, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden*

[f] *Center for Atmospheric Particle Studies (CAPS), Carnegie Mellon University, Pittsburgh, PA 15213, USA*

I. Supporting information

A. Acid-Base Titration of Succinic acid

An acid-base titration was conducted to get the logarithm of the acid dissociation constant, pK_a value, and respectively the equivalence points, where the majority of the succinic acid is singly charged for the 0.3 M solution. Starting with 20 ml of 0.3 M succinic acid ($SuccH_2$) and adding small amounts of 1.0 M NaOH, we obtained the titration curve, which is shown in Figure S1. The pK_a values for the 0.3 M pure succinic acid solution are 3.83 and 5.13 and the first equivalence point (where most of the succinic acid is singly deprotonated, $SuccH^-$) is found to be at pH = 4.48. At a pH of higher than 12, a major part of the succinic acid is fully deprotonated ($Succ^{2-}$). All pH measurements were done using a calibrated pH meter (Thermo Scientific Orion 4-Star) equipped with an Orion ROSS Ultra electrode.

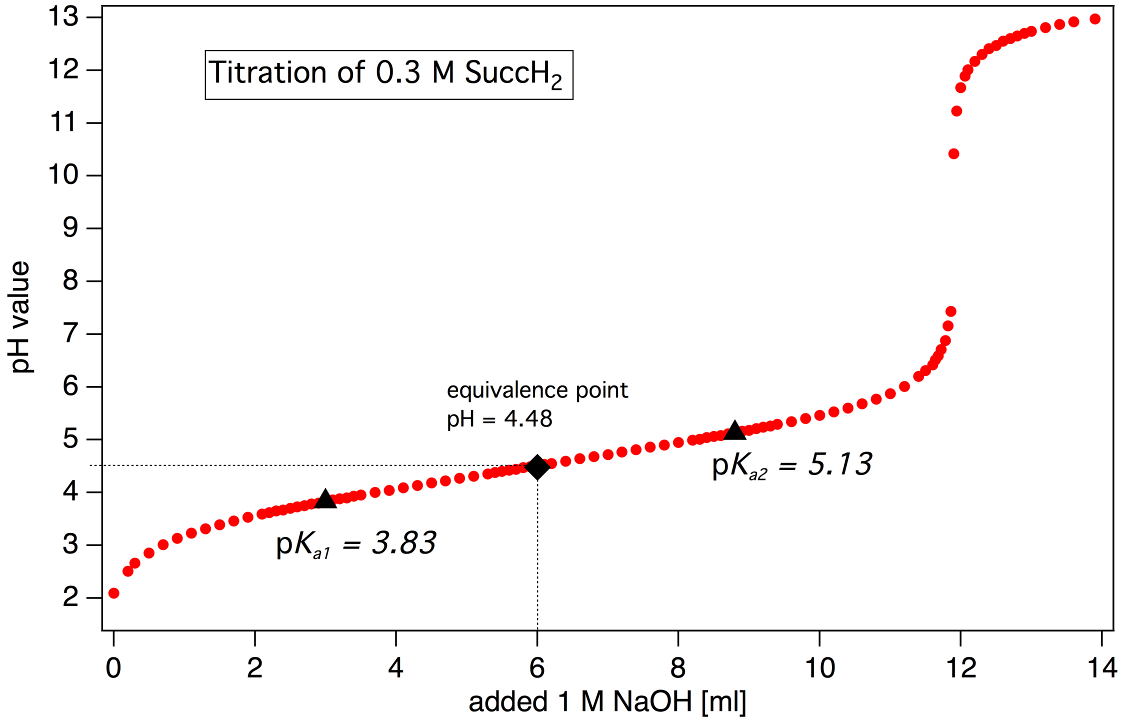

Figure S1. Titration curve of succinic acid (0.3 M aqueous solution).

B. C1s PE spectra of succinic acid at different pH

C1s core-level PE spectra, shown in Figure S2, were obtained from pure 0.3 M succinic acid solutions at 360 eV photon energy for the pH values 2.0, 4.6 and 12.9 and the binding energies of $SuccH_2$ and $Succ^{2-}$ were determined (see details in the main article). The PE intensity is displayed on an arbitrary scale as function of binding energy of the C1s photoelectrons. Note that the relative PE intensity scales of the different traces are the same. Monovalent succinate ions, $SuccH^-$, cannot be in a solution as pure species, as stated above. The spectra at pH 4.6 comprise C1s PE signal from $SuccH_2$, $Succ^{2-}$ and $SuccH^-$. While detailed analysis of the $SuccH_2$ and $Succ^{2-}$ is discussed in the main article, no further analysis could be conducted in case of $SuccH^-$. The C1s binding energies of the three different forms are too close to each other to resolve the PE lines. However, the spectrum at intermediate pH value demonstrates the changes in the PE signal due to a change in charge state of the hydrated acid. Since the spectra recorded from solutions at pH 2.0 and 12.9 do not show contributions from other protonation states, these can be considered as pure $SuccH_2$ and $Succ^{2-}$ solutions, as expected considering the pK_a values.

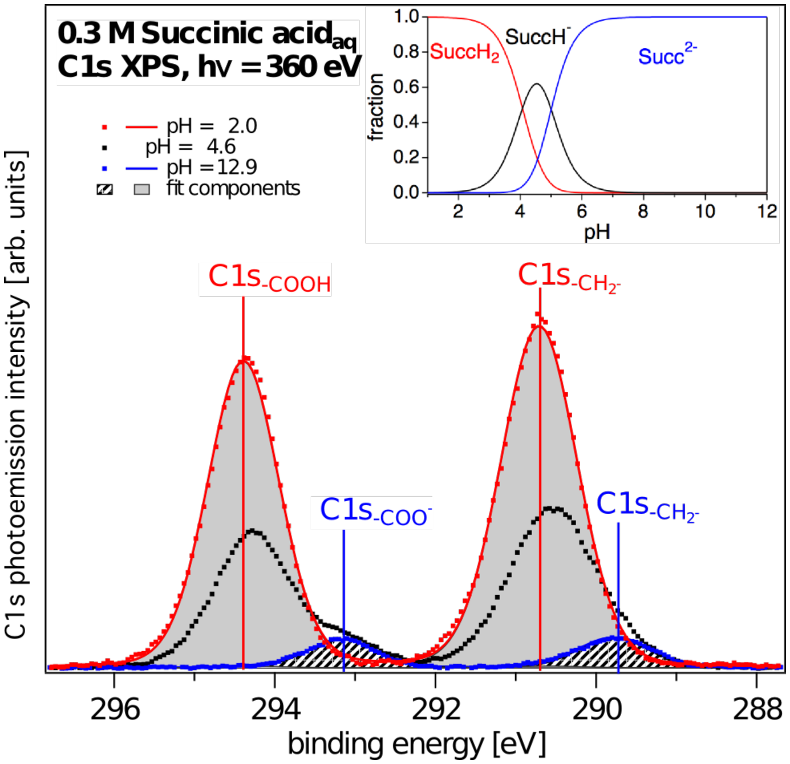

Figure S2. C1s photoelectron spectra of 0.3 M aqueous succinic acid at different pH values. Note that the relative intensity scale of the different traces is the same. Inset: Fraction of succinic acid form as function of pH value created using MEDUSA.[1]

C. Quantifying surface sensitivity using MD simulation profiles

Generally, the PE intensity at a given kinetic energy of the emitted electrons is proportional to the concentration of a compound in the probed sample volume and the photoionization cross section of the investigated species, but exponentially attenuated along its path. Investigating similar species at the same kinetic energy, their relative PE intensities are mainly dependent on their respective spatial distance from the vapor phase, which we will refer to as the species' surface propensity, and the species' surface concentration, which is also referred to as surface enrichment in the following.

To determine the relative surface enrichment for succinic acid, we need to quantify the surface sensitivity of XPS experiments on liquid micro-jets. For this purpose, the surface thickness, which is determined from MD simulation profiles, is applied in a simple model describing the surface as a layer between the air/surface and the surface/bulk interface, in which the density of the solution increases from 0 to 1 in the aqueous phase as illustrated in Figure 1 of the main article.

The surface region is assumed to be a layer between $0 \leq z \leq D$ and the bulk is from $D \leq z \leq \infty$. The PE intensity I_S, that is originating from the surface layer only, can be described in the following way:

$$I_S \sim \int_0^D e^{-\frac{z}{EAL}} dz = EAL \cdot (1 - e^{-\frac{D}{EAL}}) \; . \qquad (1)$$

The PE intensity of the bulk I_B can be described by:

$$I_B \sim \int_D^\infty e^{-\frac{z}{EAL}} dz = EAL \cdot e^{-\frac{D}{EAL}} \qquad (2)$$

Choosing a physically reasonable range for EAL of 5-10 Å[2,3] and the surface thickness extracted from MD simulation profiles, D = 4 Å, the quotient of Eq. 1 and 2 can be interpreted as the ratio of bulk to surface contribution to the total PE intensity, analogous to the sensitivity factor $\frac{n_B}{n_S}$ defined in Ref. 4 supplementary information, where the total PE signal was expressed as

$$I_{total} = I_S + I_B \sim (n_S c_S + n_B c_B) \qquad (3)$$

where c_S and c_B are the concentration in the surface region and the bulk, respectively.

$$\frac{I_B}{I_S} = \frac{1-e^{-\frac{D}{EAL}}}{e^{-\frac{D}{EAL}}} \approx \frac{n_B}{n_S} \qquad (4)$$

The resulting sensitivity factors are shown in Table S1 together with the conservative estimates mentioned in the main paper for XPS experiments on liquid micro-jets. Using the above approximation, the range of the sensitivity factors can be narrowed significantly; especially bulk contributions to the PE signal higher than 67% and lower than 45 % are excluded, which results in a significantly narrower range of possible enrichment factors, see Table S2.

Table S1. XPS sensitivity factors derived from Eq. 4, using a range of physically reasonable EAL values. The obtained estimate narrows the range for $\frac{n_B}{n_S}$ and enables the derivation of more precise surface enrichment factors of succinic acid from ratios of PE intensities.

XPS sensitivity	**Low bulk**	**High bulk**
From MD: D = 4 Å $45/55 < \frac{n_B}{n_S} < 66/33$	EAL = 5 Å 0.816	EAL = 10 Å 2.033
Conservative estimate $25/75 < \frac{n_B}{n_S} < 75/25$	0.333	3

The resulting sensitivity factors in Table S1 are used to compute enrichment factors *g* using Eq. 5 and C1s PE ratios obtained from succinic acid and succinate ions at different concentrations. These factors can be used to derive the surface concentration of a compound by multiplying the bulk concentration with *g*. Results are given in Table S2.

$$g = \frac{c_S}{c_B} = \frac{n_B}{n_S}\left(\frac{I_{SuccH2}}{I_{Succ2-}} - 1\right) \qquad (5)$$

Table S2. Surface enrichment factors of succinic acid calculated using different approaches to account for the attenuation of the PE signal, Eq. 5.

Concentration [M]	**C1s PE ratio**	**surface enrichment factors c_S/c_B**			
		25:75 to 75:25		4 Å surface thickness	
Bulk sensitivity		low	high	low	high
0.05	18.7	5.9	53.2	14.4	36.0
0.1	16.1	5.0	45.4	12.3	30.7
0.17	14.9	4.6	41.8	11.3	28.3
0.2	13.8	4.3	38.4	10.5	26.0
0.3	12.1	3.7	33.2	9.1	22.6
0.4	10.3	3.1	27.7	7.6	18.9
0.5	8.2	2.4	21.6	5.9	14.6

Rearranging Eq. 5, we find

$$\frac{I_{SuccH2}}{I_{Succ2-}} = \frac{c_S}{c_B} \cdot \frac{n_B}{n_S} + 1 \quad (6)$$

which can be used to estimate the minimum PE ratio that needs to be obtained to confirm an increased surface compared to bulk concentration ($c_S > c_B$). For this purpose we choose $n_B/n_S = 3$, indicating the least surface sensitivity estimated for this experiment (75% of the PE signal originates from the bulk of the solution). This yields $\frac{I_{SuccH2}}{I_{Succ2-}} = 1 \cdot 3 + 1 = 4$.

An observed PE intensity ratio higher than 4 indicates not only a higher surface propensity of the one studied species over another but also an increased concentration in the surface compared to the aqueous bulk. The factor 4 is determined by considering a simple surface model, see Figure 2 in the main article, in combination with the limit of the conservative estimate of 75% of the PE signal coming from the bulk. In case of an observed PE ratio of less than 4, the surface concentration compared to the bulk concentration is less or the same which means that the increased signal must come from a smaller relative surface propensity for the studied species.

References

1. I. Puigdomenech, *Chemical Equilibrium Diagrams*, http://www. kth.se/che/medusa, Accessed: March 2014.

2. N. Ottosson, M. Faubel, S. E. Bradforth, P. Jungwirth and B. Winter, *J. Electron Spectros. Relat. Phenomena* 2010, **177,** 60–70.

3. C. J. J. Powell and A. Jablonski, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* 2009, **601,** 54–65.

4. N.L. Prisle, N. Ottosson, G. Öhrwall, J. Söderström, M. Dal Maso and O. Björneholm, *Atmos. Chem. Phys.,* 2012, **12,** 12227–12242.