

Supporting Information: The Surface Composition of Amino Acid - Halide Salt Solutions is pH-Dependent

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2 Reasons for Using KCl instead of NaCl

3 Using KCl has several advantages over NaCl as the inorganic salt in our experiments for
4 several reasons. The scope of this paper is to understand how amino acids shape the ion
5 distribution at aqueous surfaces, and here we opted to use a salt that promised as little
6 difficulty as possible during the analysis of our data.

7 The primary considerations here were expected signal intensity and energy position of the
8 atomic levels. Sodium has two energy levels that are accessible with soft X-rays: Na 2s
9 (68 eV binding energy) and Na 2p (35.4 eV binding energy).¹ Na 2s is a rather weak spectra
10 feature and thus not ideal for an analysis banking on the use of fitted peak areas. The Na
11 2p levels partly overlap with the water $2a_1$ peak liquid and gas phase features. Obtaining
12 a high quality fit from the Na 2p levels would have been very difficult and would likely
13 have resulted in large error bars for the fitted peak area. The potassium 2p levels are well
14 separated from other peaks and thus a quality peak fit was relatively simple to obtain.
15 Conducting the experiment with NaCl would either take much more time (which is limited
16 by the availability of synchrotron beamtime) or would yield very large error bars obscuring
17 any possible effect in the data.

18 Fitting of Experimental Data

19 All experimental data have been fitted with Voigt profiles. Examples for the valence, Cl 2p,
20 K 2p, S 2p (if applicable) and C 1s regions are shown in figure S1. Valence band fits only
21 served the purpose to obtain the area of the $1b_1$ level of liquid water. As the valence data in
22 figure S1 a) demonstrates, the signals from multiple levels overlap in the valence region, and
23 one is forced to fit the entire valence region in order to attain the area of the liquid water $1b_1$
24 level. The sloped baselines in the fits originate from scattered electrons. The data shown in
25 figure S1 originates from the LNLS, and the experimental resolution of these measurements
26 was particularly low (compare peak width of the $1b_1$ levels from the liquid and gas phase).

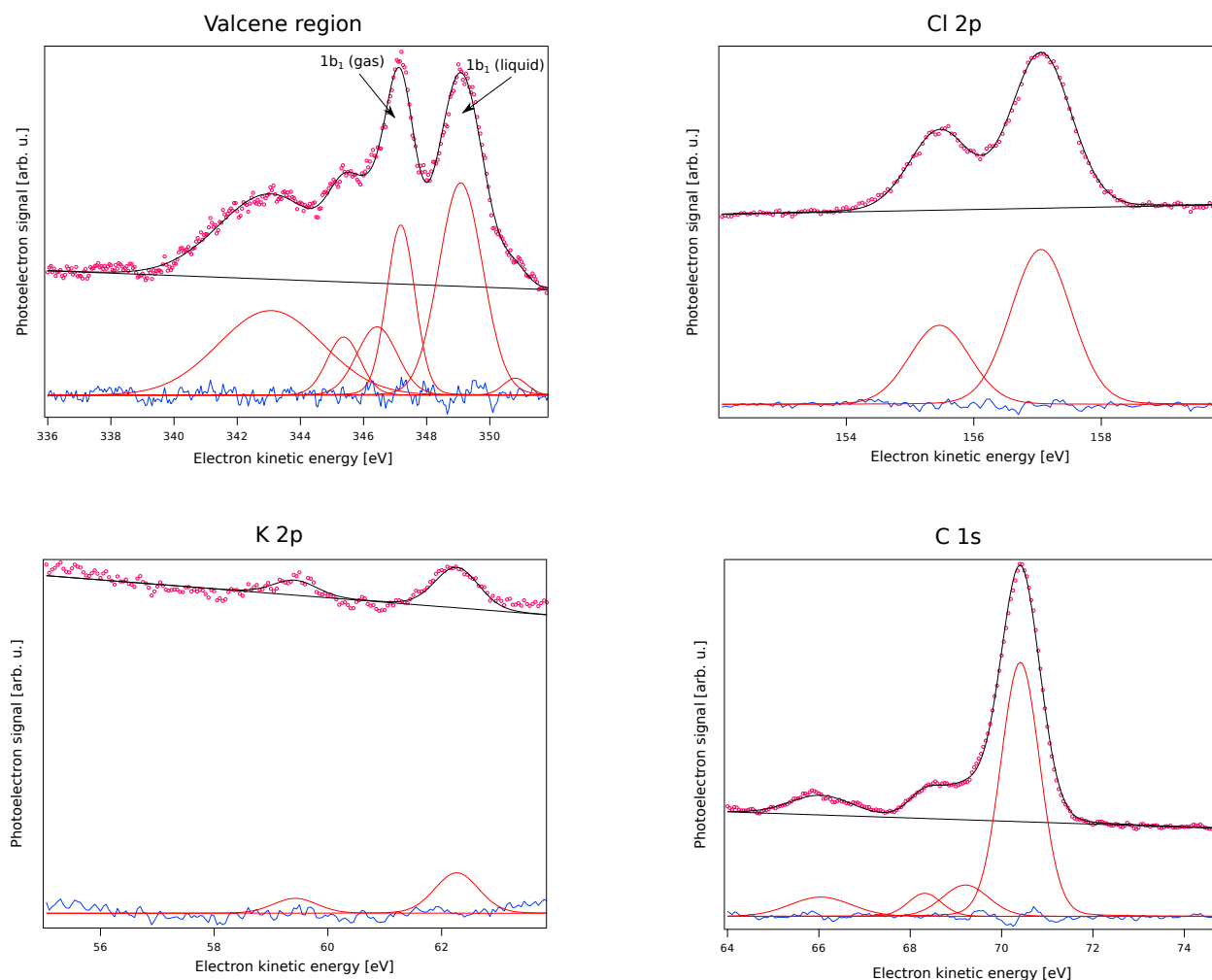


Figure S 1: The panels above depict the fits to one data set (0.1 M Phe + 0.3 M KCl solution at pH 1.8; red circles). Data shown in these panels is shown as measured. i.e. no energy calibration or normalization has been applied. The blue curve at the bottom of the figure is the fit residue, which has been used subsequently to obtain error bars.

28 Calculation of Error Bars

29 The fit errors given by the fitting packages we are using, SPAN-CF² and the Igor Pro built-
 30 in fit procedures, produce too small errors for the fit parameters. Often, even for a fit to
 31 very noisy data the errors on the fit parameters are extremely small and thus we decided to
 32 disregard these pre-build routines for the error estimation and employ a technique, which

33 produces more plausible errors. The underlying idea is that the fit residue (i.e. the real
 34 data minus the fit to it) intrinsically contains the information about the range of the fit
 35 parameters. Therefore, our starting point is the fit residue and 'extract' a range for the fit
 36 parameters.

37 The first step is to sort all values on the ordinate of the fit residue into a histogram.
 38 We decided to sort the intensity values of the fit residue into 30 bins; an example of the
 39 resulting histogram together with the fit residue is shown in figure S2 for the chloride 2p
 40 level in a 0.1 M Phe + 0.3 M KCl solution at pH 1.8. The data in the histogram was fit with
 41 a Gaussian of which the full width at half maximum (2ε) is considered to be the range of
 42 the majority of the signal fluctuations in the measured data. Note that in this approach the
 43 background noise on the data as well as contributions to the fit residue due to inadequate
 44 fits are convoluted.

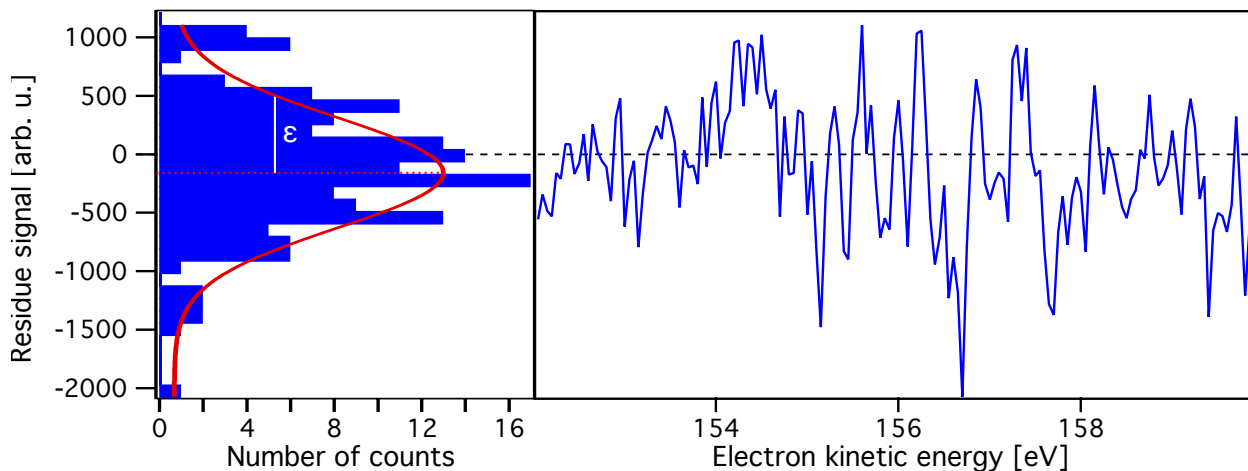


Figure S 2: This is an example of a projection of the intensity values of a fit residuum being projected into a histogram. The fit residuum shown on the right originates from the fit of two Voigt profiles to the Cl 2p level of a 0.1 M Phe + 0.3 M KCl solution at pH 1.8. The data including the fit is shown in figure 1. The data in the histogram is subsequently fit with a Gaussian, 2ε is the full width at half maximum of the Gaussian.

45 Since we consider 2ε around the fit to represent the the interval in which most of the
 46 original data points can be found, we produce two artificial data sets from ε and the original
 47 data in the following manner: In one case, we add ε to the signal in the original data and
 48 in the other case we subtract ε from the signal in the original data. The noise background

49 of the original data remains unaltered by this procedure. Note that the criterion where the
50 'signal' separates from the 'background' is arbitrary to some degree. Here, we produced a
51 linear fit using the average of the first five points and the last five points of each spectrum.
52 Only if a point of the original data is 2ϵ above that linear function, it is considered as 'signal'.
53 This method assumes that the first and last points of a spectrum only contain background
54 and no real signal, and that the background can be assumed to be a linear function. In our
55 particular case, these assumptions hold, but they are not generally true. The result of this
56 procedure for the Cl 2p level of 0.1 M Phe + 0.3 M KCl at pH 1.8 is shown in figure 3.

We fitted the artificial data sets anew, again with Voigt profiles. In these fits, we kept

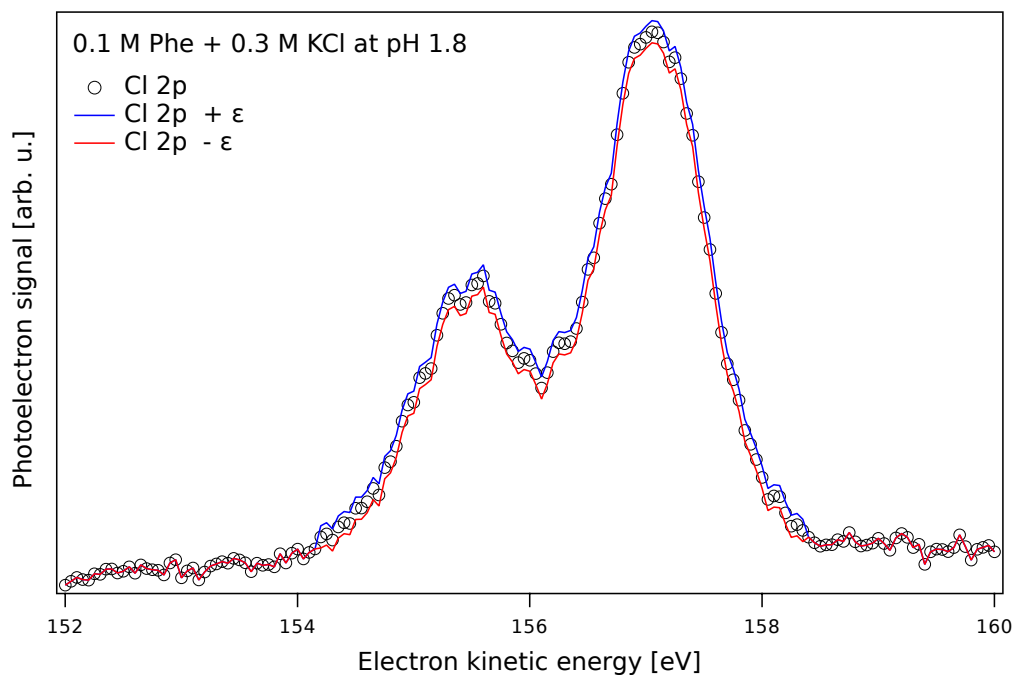


Figure S 3: The figure above shows the original data and the two artificial data sets we produced from the fit residue.

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58 the peak positions fixed to the values we obtained from the fits to the original data, so
59 that only the intensity and the broadening could vary - the two important parameters for
60 the calculation of the peak area. Finally, we compared the peak areas of the fits to the
61 original data with the two peak areas obtained from the fits to the artificial data. The larger
62 difference between the peak area of the original data and the peak areas derived from the

63 artificial data is considered to be the error.

64 Electron Mean Free Path, Probing Depth and "Surface"

65 Due to the different binding energy of the atomic levels we probed with X-rays of the same
 66 energy, the electrons originating from different levels have different kinetic energy. This
 67 results in a variation of the probing depth depending on the origin of the photoelectrons
 68 as the depth sensitivity of our method scales with the kinetic energy of the electrons. In
 69 the energy regime we employed here, the difference in probing depth is negligible when
 70 comparing the signal from K 2p and Cl 2p levels. Comparison to the water 1b₁ state yields
 71 a small difference, but this leads to the resulting factor (R_{H_2O}) underestimating the effect as
 72 the probing depth for electrons originating from the water valence band is larger. All values
 73 given in table 1 are estimates and base on the work of Thürmer et al.³

Since the electron mean free path determines the signal attenuation over a certain length,

Table 1: All numbers given for the electron mean free path (MFP) are estimates based on the work of Thürmer et al.³

Level	LNLS		BESSY II		SOLEIL	
	$\hbar\omega = 360 \text{ eV}$		$\hbar\omega = 400 \text{ eV}$		$\hbar\omega = 420 \text{ eV}$	
	E_{kin} [eV]	MFP [nm]	E_{kin} [eV]	MFP [nm]	E_{kin} [eV]	MFP [nm]
water 1b ₁	349	1.86	389	2.06	409	2.17
S 2p	197	1.30	-	-	-	-
Cl 2p	158	1.25	198	1.31	218	1.35
C 1s	71	1.20	111	1.23	131	1.24
K 2p	63	1.20	103	1.22	123	1.23

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75 our measured spectra are composed of signal originating from the surface and signal from
 76 the bulk. The majority of the signal is from the surface due to the short mean free path in
 77 comparison to the intermolecular distances. This indirectly raises the question about what
 78 the "surface" actually is in our case. Our approach here is to consider the "surface" to be
 79 the volume of the liquid, which is appreciably influenced by the presence of the amino acid
 80 layer on top, including possible charge compensation layers below in case of basic and acidic

81 solutions. As long as the amino acids are in their zwitterionic form, we do not expect the
82 formation of pronounced charge compensation layers and thus the influence of the amino
83 acid probably reaches less far into the bulk of the solution.

84 Measured Bulk pH of Sample Solutions

85 The following table lists the pH of the solutions during the measurements together with the
86 literature values for the carboxyl group of the respective amino acid. Measurements were
87 carried out with a calibrated pH meter except for the reference solution, in which case pH
88 paper was used.

Sample	$pK_a(\text{COOH group})$	acidic	no pH adjustment
0.3 M KCl (reference)		1	6
0.1 M PHE + 0.3 M KCl	2.18	1.8	5.58
0.1 M VAL + 0.3 M KCl	2.27	1.7	6.15
0.1 M MET + 0.3 M KCl	2.16	1.7	5.89
0.5 M GLY + 0.3 M KCl	2.34	1.94	6.09
0.7 M CYS + 0.3 M KCl	1.91	1.55	5.18
1 M PRO + 0.3 M KCl	1.95	1.73	6.05

89 References

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