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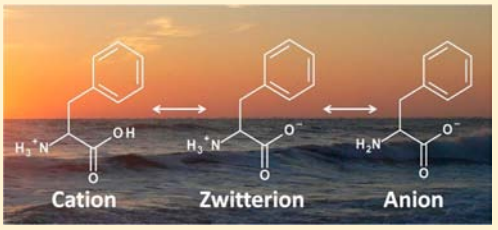
Ionization state of L-Phenylalanine at the Air–Water Interface

Elizabeth C. Griffith and Veronica Vaida*

Department of Chemistry and Biochemistry and CIRES, University of Colorado, UCB 215, Boulder, Colorado 80309, United States

Supporting Information

ABSTRACT: The ionization state of organic molecules at the air–water interface and the related problem of the surface pH of water have significant consequences on the catalytic role of the surface in chemical reactions and are currently areas of intense research and controversy. In this work, infrared reflection–absorption spectroscopy (IRRAS) is used to identify changes in the ionization state of L-phenylalanine in the surface region versus the bulk aqueous solution. L-phenylalanine has the unique advantage of possessing two different hydrophilic groups, a carboxylic acid and an amine base, which can deprotonate and protonate respectively depending on the ionic environment they experience at the water surface. In this work, the polar group vibrations in the surface region are identified spectroscopically in varying bulk pH solutions, and are subsequently compared with the ionization state of the polar groups of molecules residing in the bulk environment. The polar groups of L-phenylalanine at the surface transition to their deprotonated state at bulk pH values lower than the molecules residing in the bulk, indicating a decrease in their pK_a at the surface, and implying an enhanced hydroxide ion concentration in the surface region relative to the bulk.



INTRODUCTION

Water surfaces are ubiquitous on Earth and have long been identified as unique environments for chemical and physical processes. Surfaces are known to be important contributors to atmospheric chemistry in the modern atmosphere[1−9] and have been proposed as favorable environments for essential reactions in prebiotic chemistry.[10−15] The potential for reactions at water surfaces is influenced by the state of ionization of the reactants, thus prompting the need for a fundamental understanding of not only the ionization state of potential reactants at the water surface, but also of the ionic character of the bare water surface itself. In this work, the surface-active amino acid L-phenylalanine was used as a probe of the environment experienced by ionizable molecules in the surface region. L-phenylalanine has the unique advantage of possessing a hydrophobic group (an aromatic ring) to drive its adsorption to the surface, but also two different hydrophilic groups, a carboxylic acid and an amine base, which can deprotonate and protonate respectively depending on the ionic environment they experience at the water surface.

Numerous studies have been formulated to attempt to understand the air–water interface on a fundamental, molecular level.[4,16−26] One property of the air–water interface that has been intensely debated is the propensity of ions for the surface. This has subsequently prompted the investigation of the pK_a of molecules at the surface versus in the bulk, as well as the more fundamental problem of the pH of the bare water surface itself.[27−29] Historically, and still in many textbooks, the surface was considered to favor neutral molecules over their ionic form due to the repulsion of ionic species from the interface by an electrostatic image force.[30,31] Experimentally, this is seen as an increase in surface tension with the addition of an ionic species to water.[31] In contrast to this traditional view, more sophisticated techniques and theory in recent years have suggested that not only are some ions present at the surface, but some are actually present in excess over the bulk.[16,21,27,32−35]

Although most acknowledge there is a shift in the pK_a of molecules residing at the surface, there is no agreement on the magnitude or direction of the change. Vibrational Sum Frequency Generation (VSFG) studies have shown that long-chain acids at the surface exhibit a significant increase in their pK_a when compared to bulk solution.[36−38] A similar effect was seen with long-chain phosphates at the air–water interface using changes in surface pressure/area with changes in subphase pH.[39] In contrast, amphiphilic amino acid residues at the air–water interface (looking at the amine group only) showed a significant decrease in their pK_a compared with the bulk solution as determined by ^{1}H NMR titration.[40] In our work, L-phenylalanine contains both an acid (carboxylic acid) and base (amine) group to allow for simultaneous analysis of a high and low pK_a at the air–water interface. If the shift in pK_a at the surface is only toward the neutral form (as is indicated by the decrease in pK_a of the amine group of the amphiphilic amino acid residues[40] and the increase in pK_a of the fatty acid[36] seen in the literature), then more neutral polar group vibrational bands (i.e., more vibrations due to COOH and NH_2) relative to the bulk should be present in the surface IRRAS spectra throughout the pH range.

Further, the question as to the surface pH of water itself is far from being resolved.[33] Although anions in general are considered to have a slight propensity for the surface over cations, many think that hydronium ions (H_3O^+) are at a higher

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concentration at the surface than hydroxide ions (OH^-), yielding an acidic surface pH.[16,33] This has been experimentally confirmed by VSFG and Second-Harmonic Generation (SHG) measurements[32,41] and molecular dynamics simulations[42] for the air−water interface. A similar, but less pronounced, effect was seen at the air-ice interface.[43] Investigations performed in the colloid community using zeta potential measurements and titrations, gas collisions with aqueous microjets, as well as other molecular dynamics simulations suggest the opposite: that the water surface is basic.[33,44−48] Needless to say, the ionic nature of the bare air−water interface is of paramount importance in determining the ionization of adsorbed species. In the work presented here, the surface ionization state of L-phenylalanine, a naturally occurring amino acid used in modern biochemistry, over a wide range of pH values (pH 1−13) is identified using the *in situ*, surface-sensitive technique of infrared reflection−absorption spectroscopy (IRRAS) and subsequently compared with the same molecule's bulk phase ionization state. This allows for a direct gauge of the change in pK_a of molecules residing at the surface relative to the bulk as well as an indirect indication of the surface pH experienced by the L-phenylalanine molecules.

EXPERIMENTAL SECTION

Materials. Sodium hydroxide (NaOH, ACS grade) and hydrochloric acid (HCl, 37%) were purchased from Mallinckrodt Baker, Inc. All chemicals were used without any further purification. Stock solutions with pH values ranging from pH 0 through 14 were prepared by dissolving the appropriate amount of either sodium hydroxide or hydrochloric acid in distilled water. L-phenylalanine (99%) was purchased from Alfa Aesar, and was prepared to a concentration of 0.1 M in the stock pH solutions yielding final pH values of 0.61 (0.1 M phenylalanine in 1 M HCl), 1.62 (0.1 M phenylalanine in 0.1 M HCl), 5.67 (0.1 M phenylalanine in distilled water only), 10.56 (0.1 M phenylalanine in 0.1 M NaOH), and 13.13 (0.1 M phenylalanine in 1 M NaOH). The pH of all final solutions was recorded using a Corning 320 pH meter. For the remainder of this discussion, the bulk pH values will be referred to as their nearest whole number pH value (1, 2, 6, 11, and 13, respectively) for convenience.

Methods. *Infrared Reflection−Absorption Spectroscopy (IRRAS).* IRRAS spectra were taken using the external port of a Bruker Tensor 27 FTIR Spectrometer coupled to a Langmuir trough (NIMA Technology Ltd., U.K.). The Langmuir trough consists of a PTFE trough equipped with two computer-controlled PTFE barriers to control surface area, as well as a Wilhelmy balance to monitor changes in surface pressure. In the experiments presented here, the barriers were kept at their maximum open position (70 cm^2) for the duration of the experiment. The infrared beam exited the external port of the spectrometer and was passed through a CaF_2 focusing lens. Two 2 in. diameter gold mirrors were positioned over the trough surface to direct the focusing IR beam onto the aqueous surface at an angle of 22° relative to the surface normal, and then direct the reflected light from the surface to a liquid nitrogen cooled MCT detector. This angle of incidence is within the optimum angles found to be ideal for unpolarized light incident on an air-aqueous interface.[49] Also, with this angle of incidence using unpolarized light on an air−aqueous interface, the expected absorption bands will be negative. The spectrum resulting from this experimental setup is a reflectance-absorbance (RA) spectrum, where $RA = -\log(R/R_o)$ with R being the IR reflectivity of the surface of interest and R_o being the IR reflectivity of the background surface. These reflectivities are fully described in the literature using the Fresnel equations,[50] whose details will not be presented here. In the work presented here, spectra were collected at a 1 cm^{-1} resolution followed by averaging over 200−600 scans depending on the solution (200 scans for pH 6, 600 scans for all other pH values), using the single channel spectrum of the pH solution of interest (in the absence of phenylalanine) as the background (R_o). Before computation of the reflectance-absorbance spectrum, the single channel spectra were atmosphere corrected (subtraction of water and CO_2 lines) utilizing the OPUS software equipped to the Bruker spectrometer.

The spectra presented here remain as the resulting reflectance-absorbance spectra and are shown in Figure 2 with negative-facing peaks, while in Figure 3a.1−3a.5 the IRRAS peaks are flipped to face upward for easier comparison with the solid-state infrared spectra. Also, in Figure 2, the baselines are scaled by an additive constant to differentiate between spectra of different pH values. Finally, it is important to note that when analyzing IRRAS spectra there are residual features (appearing as positive, broad peaks) because of small changes in the structure of the water surface throughout the measurement. These features appear in every spectrum (i.e., the large positive peak seen in Figure 2 between 1600 and 1700 cm^{-1}) and should not be confused with peaks resulting from surface-residing molecules of interest.

Solid-State Infrared Spectroscopy. Solid-state spectra were obtained using the internal compartment of the Bruker Tensor 27 FTIR Spectrometer. A sample of the phenylalanine solutions at the various pH values were dried out over at least 24 h, and then were pressed into KBr pellets for solid-state analysis. The spectra were obtained with a 1 cm^{-1} resolution and were averaged over 100 scans. Although the ideal method of analysis of bulk ionization state would be direct IR spectra of the aqueous solution, due to the strong water absorption in the regions of interest solid-state analysis was performed here. It has been shown in the literature that although the infrared bands do shift according to the degree of hydration of the polar group, there is no change in the overall ionization state of the bulk molecules upon dehydration.[51] A few bound water molecules are preserved on the polar groups throughout the dehydration process, allowing for the maintenance of charge. Therefore, in the study presented here, we will use the ionization state of the dehydrated samples as representative of the bulk ionization state.

RESULTS AND DISCUSSION

Infrared reflection−absorption spectroscopy (IRRAS) was used to identify the changes in the ionization state of L-phenylalanine at the air−water interface with changes in subphase pH. L-Phenylalanine is a slightly soluble amino acid which is known to exhibit some surface activity.[52] With its large, nonpolar aromatic ring, phenylalanine has one of the highest hydrophobicity ratings of the naturally occurring amino acids.[53] From an aqueous solution, it spontaneously adsorbs to the air−water interface forming an excess surface concentration of phenylalanine molecules. The adsorption isotherms of varying pH solutions of L-phenylalanine were measured and are shown in Figure S1 in the Supporting Information. Although the kinetics of adsorption differs, the maximum surface pressure reached, and hence the surface excess concentration of L-phenylalanine molecules, is the same (within the error of the Langmuir trough surface pressure measurement) across the pH range used in this work. This surface excess is then detectable using the surface-sensitive IRRAS technique. Amino acids have two polar groups, a carboxylic acid and an amine, allowing for their progression through three different ionization states with changes in pH in an aqueous solution: cation at low pH (protonated amine, neutral carboxylic acid), zwitterion at intermediate pH (protonated amine, carboxylate anion), and anion at high pH (neutral amine, carboxylate anion), structures illustrated in Figure 1. In bulk aqueous solution, amino acids exist primarily as zwitterions throughout a very broad pH range, encompassing environmentally relevant pH values.[54−56]

Assignment of Polar Group IRRAS Bands. Figure 2 shows IRRAS spectra of phenylalanine at the air−water interface at three different subphase pHs progressing from

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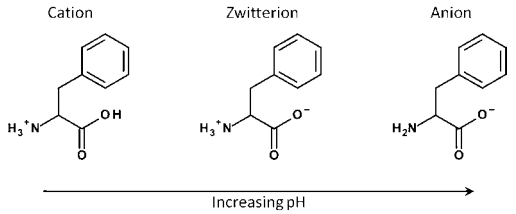

Figure 1. Change in ionization state of the polar groups of L-phenylalanine with changes in pH.

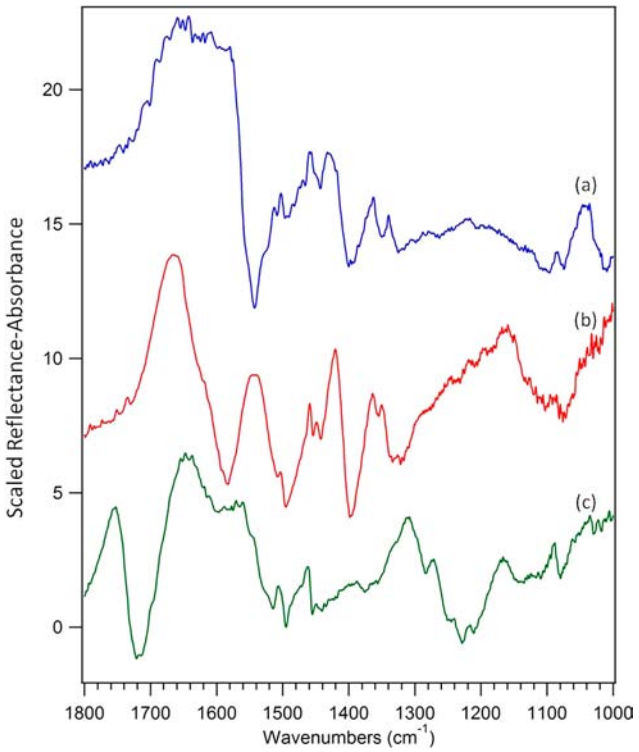

Figure 2. IRRAS spectra of L-phenylalanine at the air–water interface at bulk pH values of (a) pH 13 (blue), (b) pH 6 (red), and (c) pH 1 (green).

pH 13 in blue (Figure 2a), to pH 6 in red (Figure 2b), and finally to pH 1 shown in green (Figure 2c). From this pH progression as well as from both IRRAS[57] and solid-state[51,58–60] infrared literature comparison, the polar group vibrational modes are assigned as presented in Table 1. Detailed studies have been made of stearic acid (a carboxylic acid with an 18-carbon long hydrocarbon chain) at the air–water interface using the IRRAS technique,[57,61–63] but only limited information is available about primary amines due to experimental difficulties.[64,65] While absorption bands due to N–H groups in both primary and secondary amides have been reported using IRRAS, none from amines have ever been observed.[64] This absence has been attributed to either the difference in the nature of the bonds themselves,[64] or to a simple unfavorable orientation of those modes relative to the surface to be observed using the IRRAS technique.[64,65] Tilting of the transition moments of vibrations relative to the surface normal could result in either weakening or the complete absence of these bands from the resulting IRRAS spectrum, which may have been the case in the attempted IRRAS spectra of long-chain primary amines at the surface.[65] Therefore, direct comparison of the spectra presented here with literature IRRAS spectra could not be made for identification of the amine state of ionization, thus assignments were made through comparison with solid-state spectra of phenylalanine[51,58] and other amino acids.[59,60]

Table 1. Summary of Polar Group Assignments from the IRRAS Spectra of L-Phenylalanine Shown in Figure 2 at the Indicated Bulk pH Values

pH 1 cation	pH 6 zwitterion	pH 13 anion	assignments[51,57–61]
1717	-	-	ν (C=O)
1600	-	-	β_{as} (NH_3^+)
-	1583	1542/1522 (sh)	ν_{as} (COO^-)
1530 (sh)/1514	1507	-	β_s (NH_3^+)
-	1396	1397	ν_s (COO^-)
-	-	1349	γ_s (CH_2) + β_s (NH_2)
1284	1284	-	ρ (NH_3^+)
1140	1140	-	ρ (NH_3^+)

Beginning with the carboxylic acid group assignments, the neutral carboxylic acid C=O stretch is experimentally observed in the pH 1 IRRAS spectrum at 1717 cm^{-1}. This assignment was made through comparison with the neutral carboxylic acid C=O stretch of stearic acid at the air–water interface using IRRAS spectra taken and assigned by Gericke and Hühnerfuss.[57] As the pH increases, the carboxylic acid group is deprotonated resulting in two carboxylate stretches. At a subphase pH of 6, ν_{as} (COO^-) is observed at 1583 cm^{-1} and the symmetric stretch ν_s (COO^-) is observed at 1396 cm^{-1}. At pH 13, the antisymmetric stretch is shifted to lower energy at 1542 cm^{-1} with a shoulder at 1522 cm^{-1}, while the symmetric stretch is observed at 1397 cm^{-1}. The symmetric stretch frequency agrees well with the literature,[57] as do both of the antisymmetric stretch frequencies.[57,66] The shift in the antisymmetric carbonyl stretch between pH 6 and pH 13 has been attributed to differences in hydration seen experimentally in the splitting of the antisymmetric carbonyl vibration observed in fatty acid studies.[66] Hydrogen bonding is known to shift carbonyl stretches to lower frequency,[62,66] and thus, if a change in hydration of the carbonyl group occurs between these two pH values, such a shift would be expected to occur.

The amine group assignments are more difficult. Only one peak was observed and assigned to the neutral amine group: the combination band arising from the symmetric out-of-plane phenyl ring CH_2 bending mode (γ_s (CH_2)) and the symmetric NH_2 bending mode (β_s (NH_2)) at 1349 cm^{-1} observed only in the pH 13 spectrum. This peak was assigned through comparison with solid-state spectra of anionic L-phenylalanine in the literature.[51,58] The protonated amine vibrations were more apparent. At pH 1, the antisymmetric NH_3^+ bend was observed weakly at 1600 cm^{-1}, the symmetric bend at 1514 cm^{-1} with a shoulder at 1530 cm^{-1}, and two NH_3^+ rocks at 1284 and 1140 cm^{-1}.[59,60] At pH 6, only the symmetric bend was observed at 1507 cm^{-1}, as well as the two NH_3^+ rocks at 1284 and 1140 cm^{-1}.

The pH 1 IRRAS spectrum also shows a strong enhancement in three peaks centered around 1228 cm^{-1}. These peaks are not due to the amine or the carboxylic acid group on the phenylalanine molecules, and are instead attributed to nonpolar moiety vibrations.[51,67] This enhancement could be due to a change in orientation of the hydrophobic aromatic ring of the phenylalanine molecules residing at the surface due to the transition of the polar groups to a cationic form at this low

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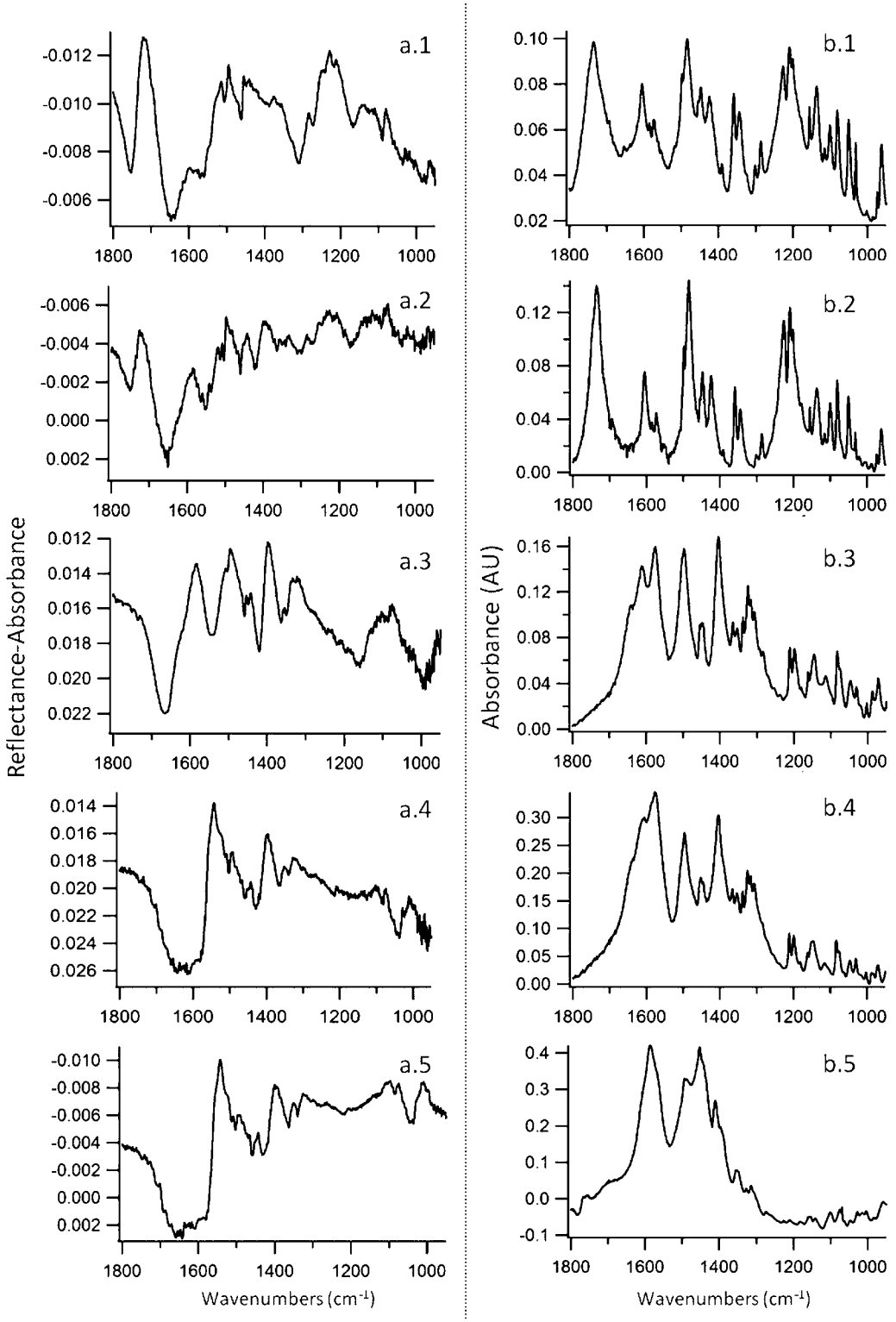

Figure 3. Comparison of IRRAS spectra (a.1−a.5) with peaks flipped for clarity (upward facing peaks) with solid-state infrared spectra (b.1−b.5) of L-phenylalanine at bulk pH 1 (a.1, b.1), pH 2 (a.2, b.2), pH 6 (a.3, b.3), pH 11 (a.4, b.4), and pH 13 (a.5, b.5). It is clear from this series of spectra that at the extreme pHs there are differences between the surface IRRAS spectra and the bulk solid-state spectra indicating differing molecular ionization states, while at the intermediate pH of 6 similar spectral features are observed in both (a.3 and b.3) indicating identical molecular ionization states. Between pH 1 and pH 2 the bulk solid-state spectra exhibit the same spectral features (b.1 and b.2), while the surface IRRAS spectra show some spectral changes (a.1 and a.2). Further, at high pH, although the spectral features change between pH 11 and 13 in the bulk solid-state spectra (b.4 and b.5), there is no change in the surface IRRAS spectra (a.4 and a.5). These spectral changes are summarized and correlated with molecular ionization states in Table 2.

subphase pH value. IRRAS is a technique which is sensitive to orientation at the surface, and intensity changes have been previously attributed to an orientational change at the interface.[68,69] As the intensity of IRRAS absorption bands is a

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Table 2. Ionization State of Surface and Dried-from-Bulk L-Phenylalanine Molecules from the IRRAS and Solid-State Infrared Spectra Presented in Figure 3

pH	IRRAS COOH/COO^-	IRRAS NH_2/NH_3^+	surface ionization state	bulk ionization state
1	COOH	NH_3^+	cation	cation
2	COOH and COO^-	NH_3^+	cation and zwitterion	cation
6	COO^-	NH_3^+	zwitterion	zwitterion
11	COO^-	NH_2	anion	zwitterion
13	COO^-	NH_2	anion	anion

complex quantity depending on many different variables, it is difficult to assign this intensity enhancement conclusively.

Comparison of Surface versus Bulk Ionization State. Using the assignments made from the IRRAS spectra (Figure 1 and Table 1), the ionization state of phenylalanine at the air−water interface at other intermediate subphase pHs could be made (Figure 3a.1 − 3a.5, tabulated in Table 2). IRRAS spectra at various subphase pHs from 1 through 13 are shown on the left-hand side of Figure 3 (a.1−a.5). At pH 1, phenylalanine exists as a cation at the surface. At pH 2, phenylalanine was observed as both a cation and as a zwitterion at the surface. At pH 6, only the zwitterion form of phenylalanine was observed. Finally, at pH 11 and 13, only the anion form of phenylalanine was observed at the surface. The right-hand side of Figure 3 (b.1−b.5) show solid-state infrared spectra of samples dried from bulk solutions of the same subphase pH as the corresponding IRRAS surface spectra. The ionization state of phenylalanine in these spectra (Table 2) was identified through comparison with literature spectra.[51,58] This allows for comparison between the ionization state of phenylalanine at the water surface with that in the bulk solution. Through this comparison, it becomes apparent that there is, in fact, a difference in the ionization state of phenylalanine at the surface compared with the bulk. The ionization states agree at a bulk pH of 1, 6, and 13, but do not agree at pH 2 or pH 11. At pH 2, the surface shows both the cationic and zwitterionic form of phenylalanine while the bulk spectrum only shows the cationic form. At pH 11, the surface phenylalanine molecules are anions only, whereas the bulk molecules are zwitterions.

This difference in ionization state gives insight into the surface pK_a of the polar groups of L-phenylalanine relative to the bulk. The polar groups of the molecules at the surface transition to their deprotonated state (NH_3^+ to NH_2, and COOH to COO^-) at a lower bulk pH than the polar groups of the molecules in the bulk. This illustrates a decrease in the pK_a of the polar groups at the air−water interface relative to the polar groups in the bulk. Others have proposed that this shift in pK_a is simply toward more neutral molecules,[70] but this is not seen here. Since there is a shift to the conjugate base of the respective polar groups at a lower pH than in the bulk, the pK_a of both the carboxylic acid group and the protonated amine group of L-phenylalanine are lowered at the interface. Although the shift in pK_a of the protonated amine group does favor the un-ionized polar group, the carboxylic acid group actually transitions toward more ionic species (more carboxylate anions) at the surface. It is difficult to quantify this change in pK_a using the IRRAS technique due to the complex composition of the peak intensities, but the qualitative change between the bulk and surface ions is clear.

Indirectly, the transition to the conjugate bases of the polar groups at the surface at lower pH values also indicates that the surface pH is higher than the bulk pH in the presence of L-phenylalanine. Physically, phenylalanine molecules see a higher propensity for OH^- ions at the surface compared with H_3O^+ ions. The ionic nature of the bare water surface is an area of great interest, currently with much controversy.[16,33] IRRAS allows for the indirect observation of the ion propensity for the surface through the transition between ionization states of ionic species at the air−water interface as seen here with phenylalanine. The presence of ionic species at the surface does disrupt the structure of the water surface itself.[4,71−77] Therefore, although it is not possible to comment on the pH of a neat water surface using solely the results presented here, this work does show a chemically relevant change in surface pH versus the bulk aqueous solution in the presence of an adsorbed organic molecule.

It is important to note that the IRRAS technique allows for analysis of molecules in the surface region, but is not limited to the region of noncentrosymmetry. In fact, the probe depth of IRRAS has been reported to be as large as 1−2 μm.[78] Surface-sensitive techniques such as VSFG and SHG have much smaller probe depths,[79] but this depth varies depending upon the molecules residing at the surface: ions present at the surface have been seen to increase the interfacial depth.[72,80] It is possible that the difference seen in the direction of the shift of the surface pK_a in this work compared with other studies as well as the implied higher OH^- concentration may be attributed to this difference in surface region probed. It has been proposed that since many of the strictly surface-layer spectroscopic techniques (VSFG, SHG) show an increased hydronium (H_3O^+) concentration at the surface, there must then be a complementary hydroxide (OH^-) rich subsurface layer to maintain charge-neutrality.[33] The probe depth of the IRRAS technique is greater than the probe depth of VSFG,[78] and could therefore be sampling this under-layer as well as the surface layer, leading to the observation of a higher OH^- concentration and decreased pK_a. Regardless, the surface region sampled using IRRAS of L-phenylalanine molecules in this work is the reactive region of interest, as evidenced by the difference in surface vs bulk ionization state of phenylalanine observed.

Finally, it is apparent from many studies of the water surface that it is a complicated environment that is not yet fully understood. Some of the controversy in the literature regarding the ionic nature of the surface of water itself as well as the pK_a of surface-residing species is likely due to a complex combination of the use of different molecular probes, different techniques, as well as different experimental conditions. The environment experienced by molecules residing at the surface is complex and dependent upon many of these interworking factors. For example, the compression state of the monolayer affects the orientation of the polar groups at the interface, which then can affect the hydration state of the polar groups themselves through the restricted availability of surface water molecules. The hydration state of the polar groups can thus influence the propensity for ion formation. Thus, directly comparing studies of water-soluble molecules such as L-

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phenylalanine, that merely have a surface excess concentration, with surfactants such as stearic or palmitic acid that reside solely at the interface anchored by a long hydrophobic tails, can be problematic. Each of these molecules orients itself differently and has a different compression state at the surface, and thus its polar groups are exposed to different environments. Further, as discussed earlier, the technique used to probe the water surface can be probing different molecular environments merely by the depth into the bulk solution that they penetrate. Therefore, although the findings in this work do not agree with all of the literature studies performed previously with different techniques and different molecules, it adds a unique probe to the overall understanding of water surfaces. L-phenylalanine, with both an acid and base group, was shown in this work to experience a hydroxide-rich environment in the surface region as probed by the *in situ*, surface-sensitive technique IRRAS, and to exhibit a lowering of the pK_a of both of its polar groups at the surface relative to the bulk.

CONCLUSIONS

In this study, the ionization state of the hydrophobic amino acid L-phenylalanine was identified *in situ* in the surface region using the surface sensitive technique IRRAS, and was subsequently compared to the ionization state of bulk molecules through a range of bulk pH values (pH 1−13). Through the use of an amino acid containing both an acid and base polar group, it was shown that both of the polar groups of the molecules residing in the surface region transitioned to their deprotonated state at a lower pH than the molecules in the bulk. This indicates directly a decrease in the pK_a of the polar groups at the interface and indirectly a higher propensity of OH^- for the surface region. More broadly, it is apparent from both this study as well as the cited literature that the ionization state at the surface is qualitatively different from the bulk. The increased acidity of polar groups at the interface observed in this work subsequently has consequences on the chemistry these molecules are capable of performing.

ASSOCIATED CONTENT

Supporting Information

Adsorption isotherms of L-phenylalanine to the air−water interface at varying bulk pH values demonstrating surface propensity. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: vaida@colorado.edu

Notes

The authors declare no competing financial interest.

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