James Madison University
JMU Scholarly Commons

Senior Honors Projects, 2010-current

Honors College

Spring 2015

Effects of anions and amino acids on surface tension of water

Diana Al Husseini
James Madison University

Follow this and additional works at: https://commons.lib.jmu.edu/honors201019

Part of the Physical Chemistry Commons

Effects of Anions and Amino acids on Surface Tension of Water

_____

An Honors Program Project Presented to

the Faculty of the Undergraduate

College of Science and Mathematics

James Madison University

_____

in Partial Fulfillment of the Requirements

for the Degree of Bachelor of Science

_____

by Diana Al Husseini

May 2015

Accepted by the faculty of the Department of Chemistry and Biochemistry, James Madison University, in partial fulfillment of the requirements for the Degree of Bachelor of Science.

FACULTY COMMITTEE: HONORS PROGRAM APPROVAL:

_____   _____
Project Advisor: Yanjie Zhang, Ph. D.,   Philip Frana, Ph.D.,
Assistant Professor, Chemistry   Interim Director, Honors Program

_____
Reader: Gina MacDonald, Ph. D.,
Professor, Chemistry

_____
Reader: Kevin Caran, PhD.,
Associate Professor, Chemistry

Table of Contents

List of Figures

List of Tables

Table 5. Densities (g/cm^3) of different amino acids collected my Anton Paar DMA 4500 density meter.

Table 6. Surface tension increments of amino acids at different pH solutions.

Table 7. Percent composition of different groups of glycine according to Henderson-Hasselbalch equation.

Table 8. Percent composition of different groups of alanine according to Henderson-Hasselbalch.

Table 9. Percent composition of different groups of serine according to Henderson-Hasselbalch equation.

Acknowledgements

I would like to thank my research advisor, Dr. Yanjie Zhang, for all her support, guidance and advising throughout my undergraduate years at James Madison University. I would also like to thank my honors committee members, Dr. Gina MacDonald and Dr. Kevin Caran, for reviewing my thesis. In addition, I would like to acknowledge all the members in Zhang's group for their support during my undergraduate years at James Madison University.

Abstract

Hofmeister series is a set of ions in order of their abilities to affect physical properties in aqueous solutions. Franz Hofmeister was the first to discover the specific ion effects on protein solubility in aqueous solutions. Although the Hofmeister phenomena are general, their mechanisms are still not fully understood. Herein, we use optical tensiometry by a pendant drop method to study the Hofmeister anion effects on the surface tension of water. It has been observed that the surface tension of water increases linearly as the salt concentrations increase. The effects of salts follow a specific trend with respect to the surface tension increments: $SO_4^{2-} > CO_3^{2-} > H_2PO_4^- > F^- > Cl^- > Br^- > I^- > NO_3^- > ClO_4^- > SCN^-$. Using the same method, the effect of solution pH and amino acids ions on the surface tension of different amino acid solutions is also being investigated. So far the surface tension measurements of glycine, L-alanine and L-serine suggest that the surface tension increases due to the abundance of ionic species comparing to the neutral species and the hydrophobic chains. These studies will provide us with some valuable data that would help further the understanding of the behaviors of salts and amino acids at the air/water interface.

Introduction

It is said that Hofmeister's contribution to the field of electrolyte chemistry is as important as Mendel's contribution to genetics.[1] The name "Hofmeister" is especially remembered when talking about the specific series of ions called Hofmeister series. In 1888, Franz Hofmeister discovered groups of cations and anions that behave in a specific order when present in protein mixtures. He observed this intriguing phenomenon when testing the precipitation power of these ions toward globulin and albumin found in dissolved egg white mixture.[2] In collaboration with two of his students S. Lewis and R. Limbeck, Hofmeister published a series of six papers regarding the mechanisms of Hofmeister series in aqueous solutions.[1] Some examples portraying physical behavior in aqueous solutions that follow Hofmeister order are: enzyme activity, micelle formation, protein stabilization and optical rotation of sugars and amino acids.[3, 6-11] Such behaviors are more affirmed by anions rather than cations.[7, 12] A typical order of the anions in the Hofmeister series is shown in Figure 1. The behavior of Hofmeister anions can be divided into two main groups: Kosmotropes and Chaotropes. Kosmotropes are on the left of chloride while Chaotropes are on the right of chloride.[7] Chloride is considered as the dividing line between the two groups.[3] Kosmotropes are usually small and well-hydrated ions which favor stabilization and salting out of proteins.[14] Chaotropes, on the other hand, are large and less favorably hydrated ions which leads to the destabilization and salting in of proteins.[14]

Although the Hofmeister series has been known for decades, their mechanisms are still under study and debate. There have been many hypotheses stated; earlier hypotheses suggested that Hofmeister ions have the ability to make and break hydrogen bonds in the bulk of water while more recent studies suggest that their mechanisms are directly related to their adsorptive
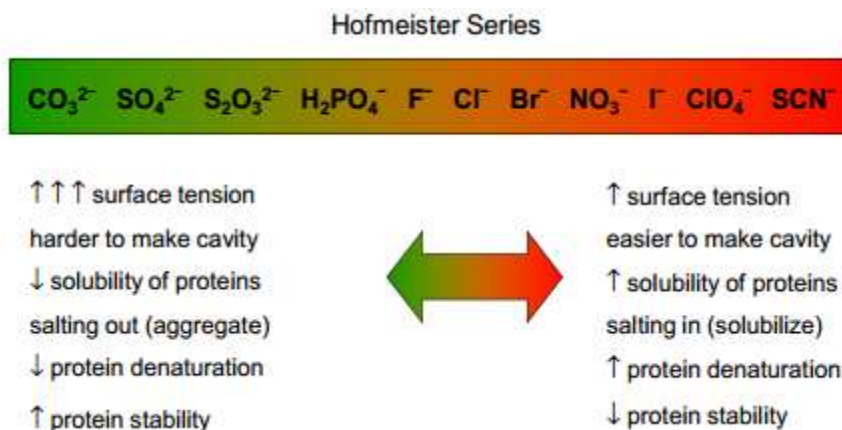
Figure 1. Hofmeister anions and their specific ion effects in different aqueous solutions. [3]

behavior at the interface. [3, 5,6, 7, 13] Since recent studies suggest strongly that ions might not be able to affect hydrogen bonding beyond the first hydration shell, there have been plenty of studies showing the specific ion effect on the interface rather than the bulk of the solution due to their physical properties. [15,16] For example, Yang and Zhao studied the Hofmeister effect on the interfacial dynamics of single molecules where the good correlation between the amplitude of the surface friction and the surface tension increment showed that Chaotropes enhance the hydrophobic interaction unlike the Kosmotropes. This is due to the water ordering and the high charge density properties of the Kosmotropes unlike choatropes. [17] Similar conclusions were made by Nathaniel Nelson and Daniel K. Schwartz. [18] Molecular Dynamic simulations were done by Jonathan N. Sachs and his group where it was hypothesized that Chaotropes are more likely to disturb the water structure at the interface due to their large size. [19] Polarizability could also have a major effect according to Eric Brown and his colleagues. This is because the electron cloud distortion of any chemical species has the ability to make the surface location favorable and interaction of water plausible at the interface. [20] In addition, energies like Gibbs free energy, entropy and enthalpy of hydration or dehydration can also explain the specific ion effect. Laurel

Pegram and Tom Record found a correlation between partition coefficients and Gibbs free energy of dehydration of different Hofmeister ions.[21]The higher the dehydration energy is, the lower the partition coefficients for partitioning of ions between bulk and the air-water interface which in turn increase the surface tension water.[21]

Herein, our research interest is to explore the effects of anions on the surface tension of water as well as the interfacial tension at the hydrophobic/aqueous interfaces with different polarity. We have set up the experiments to measure the surface tension of water in the presence of salts by using pendant drop method on an optical tensiometer. However, the experiments to measure the interfacial tension at the hydrophobic/aqueous interface have not been successful. There are several possible reasons for the unsuccessful experiments at the hydrophobic/aqueous interface including unstable volume of the drop, high viscosity of dodecane, and the interference resulting from the impurities in dodecane. Inspired by the Hofmeister series experiments, we decided to investigate the effects of amino acids on the surface tension of water at different pH solutions using the same instrumentation and methods. We are currently exploring how the amine, carboxyl and R groups of different amino acids change the surface tension of water at different pH values. These different groups can be charged or neutral depending on their pK_a and the pH of the medium. Our simple model system allows us to obtain valuable data that would help further understanding of how different parts of amino acids interact with water at the air/water interface. Understanding the behavior of different amino acids is important for some recent applications in the biomedical field involving natural and biodegradable amino acids based surfactants, drug delivery tools and modifiers of the physiochemical and biological properties of biomaterials.[22]

Experimental

Methods

Attention Theta optical tensiometer shown in Figure 2a was used to conduct surface

tension related experiments. This instrument is a programmable video based instrument designed

for measuring various physical properties like static and dynamic contact angles, surface free

energy of solids and dilatational interfacial rheology. The radiation source is LED based light

which helps to assure a sharp image with minimal sample heating. The back enclosed part of

Theta contains a camera which is adjusted to capture 60 photos per second (60 fps) at a

resolution of 640×488 pixels. For our experiments, we adjusted the fps to 33% which is around

20 fps. We record each trial for 30 seconds after the drop suspension. Each concentration of a

particular solution, whether it contained anions or amino acids, was recorded three to four times.

The average of the trials is then calculated and plotted with respect to the different

concentrations. An automatic single liquid dispenser is used to suspend a drop containing

aqueous phase of different Hofmeister series anions or amino acids. The instrument measures the

surface tension by drop shape. It is important to suspend maximum volume drop which is usually

around 10.00 μl depending on the nature of the solution and its concentration. This volume

maintains the balance between the two forces acting on the drop: gravitational force and surface

tension.

Theta tensiometer measures surface tension using Laplace equation, which describes the

pressure difference across a curved interface: [23]

$$ \gamma = (1/R_1 + 1/R_2) = \Delta p = \Delta p_0 + \Delta \rho g z \qquad \text{eq. 1} $$

where γ is the surface tension, R_1 and R_2 are the two principal radii of the curvature of the

interface, Δp is the pressure difference across the interface, Δp_0 is the pressure difference at the

drop apex, $\Delta\rho$ is the density difference between the glass melt and air and g is the gravitational

acceleration constant. Instead of the distance z, the curvature (s) is taken into consideration for

the pendent drop (Figure 2b). A more simplified equation is given as:

$$\gamma = \Delta\rho g R_0^2 / \beta \qquad \text{eq. 2}$$

where R_0 is the radius of drop curvature at apex and β is the capillary constant and is defined by

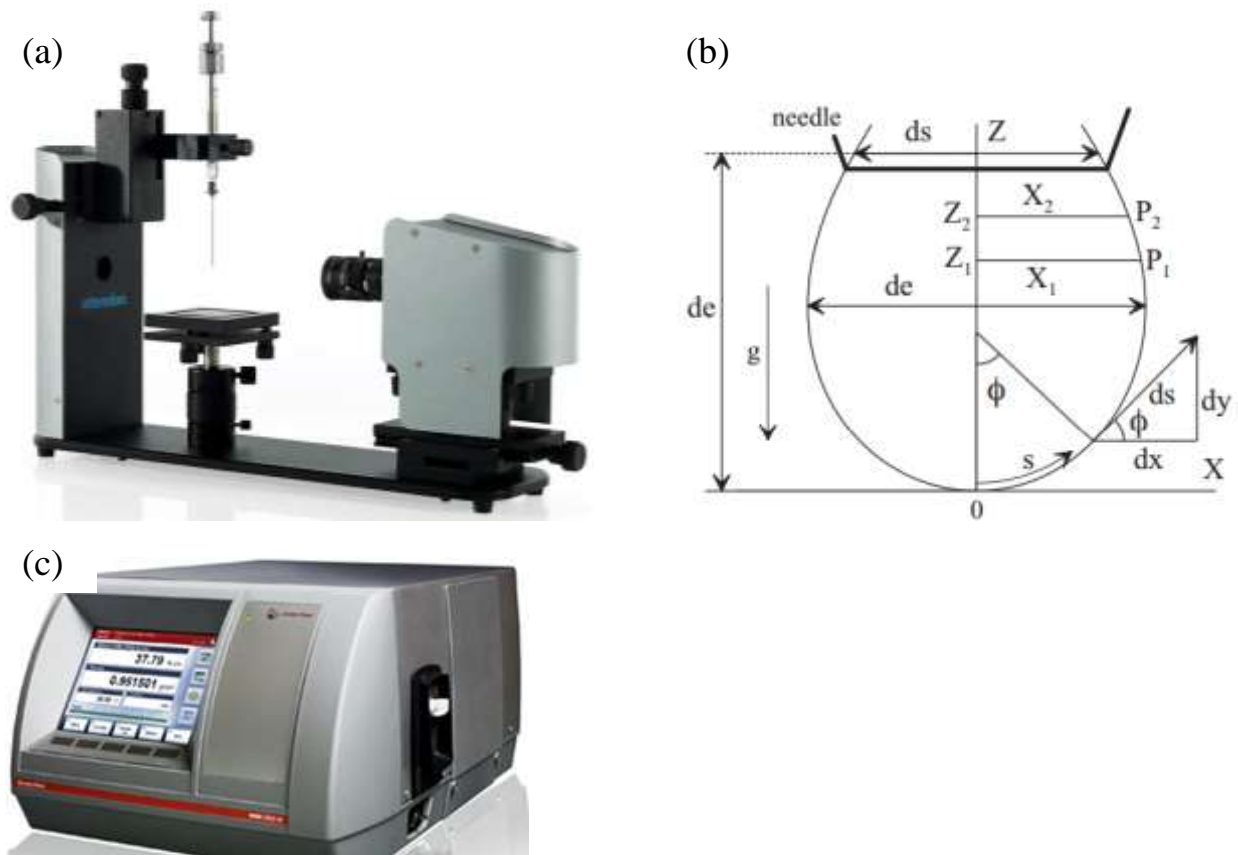$\Delta\rho g R_0^2 / \gamma$.

(a)

(b)

(c)

Figure 2. (a) Attention Theta Optical tensiometer. (b) Illustration of the drop curvature. (c)

Anton Paar DMA 4500 density meter.

Anton Paar DMA 4500 density meter shown in Figure 2cb was used to measure accurate

densities for the aqueous solutions of different concentrations at 25ºC. The sample is introduced

into U-shaped tube that is electronically excited to oscillate at its characteristics frequency. The characteristic frequency changes depending on the density of the sample. Via a precise determination of the characteristic frequency and an appropriate adjustment, the density of the sample is determined. Anton Paar DMA 4500 measures the densities of the liquid samples at wide range of temperatures with accuracy of 0.00005 g/cm^3 and $0.03°$C. The density of salt solutions at each concentration is measured at least three times and the average was taken. The density meter reads five digits after the decimal point and usually only the last digit varies between trials.

Surface Tension of Salt Solutions

The following salts were used for the experiments: Na_2CO_3, Na_2SO_4, NaH_2PO_4, NaCl, NaBr, $NaNO_3$, NaI, $NaClO_4$, and NaSCN. The concentrations started at 0.2 M with an increment of 0.2 M reaching to 2.0 M except for Na_2SO_4 where the maximum concentration can be reached was 1.4 M. The surface tension measurements were done at 25 $°$C.

Surface Tension of Amino Acid Solutions at Varied pH values

The amino acids used were glycine, L-alanine, and L-serine at pH values 2, 4, 7, 9 and 11. The concentrations for individual amino acids ranged from 0.2 M to 1.0 M with an increment of 0.2 M. The pH was adjusted manually using very concentrated sodium hydroxide for basic solutions and hydrochloric acid for acidic solutions. The surface tension measurements were also done at 25 $°$C.

Results and Discussion

Surface Tension of Salt Solutions

In order to measure the surface tension of the salt solutions it is necessary to obtain their densities at different concentrations. Table 1 listed all the density data collected on an Anton Paar DMA density meter for the nine salts studied.

Table 1. Densities (in g/cm^3) of salt solutions measured by Anton Paar DMA 4500 density meter at 25°C.

Salts Conc. (M)	Na$_2$CO$_3$	Na$_2$SO$_4$	NaH$_2$PO$_4$	NaCl	NaBr	NaNO$_3$	NaI	NaClO$_4$	NaSCN
0.2	1.01854	1.02223	1.01488	1.00552	1.01317	1.00835	1.01976	1.01283	1.00529
0.4	1.03902	1.04558	1.03208	1.01349	1.02859	1.01942	1.04226	1.02856	1.01331
0.6	1.05904	1.07011	1.04926	1.02147	1.04364	1.03046	1.06490	1.04409	1.02134
0.8	1.07877	1.09333	1.06601	1.02933	1.05961	1.04146	1.08744	1.05967	1.02947
1.0	1.09756	1.11582	1.08270	1.03725	1.07765	1.05197	1.10647	1.07473	1.03706
1.2	1.11609	1.13816	1.09920	1.04504	1.09050	1.06286	1.13237	1.09012	1.04503
1.4	1.13446	1.16014	1.11517	1.05261	1.10568	1.07364	1.15472	1.10574	1.05279
1.6	1.15259	*	1.13121	1.06042	1.12123	1.08429	1.17704	1.12039	1.06078
1.8	1.17018	*	1.14662	1.06778	1.13433	1.09473	1.19926	1.13634	1.06811
2.0	1.18838	*	1.16254	1.07564	1.15170	1.10579	1.22137	1.14988	1.07600

Surface tension of salt solutions at varied salt concentrations is shown in Figure 3. It can be observed that the surface tension increased linearly with increasing salt concentration. The data are fitted into a linearly function:

$$\gamma = \gamma_0 + \sigma C \qquad \text{eq. 3}$$

where γ is the surface tension of salt solution, γ_0 is the surface tension water in the absence of salts, C is the molar concentration of the salt, and σ is the surface tension increment in

mN m^{-1}M^{-1}. The fitted surface tension increments, σ, for all the salts studied herein are compiled in Table 2 together with some available literature values. The data collected follow the Hofmeister series which was established by Franz Hofmeister and are consistent with the literature.[5,23,24] The different surface tension increments can be correlated to the different physical properties of the salt such as ion size, hydration number, ion polarizability, and Gibbs free energy found in Table 3. Recently, it has been suggested that the first hydration shell of the solution is influenced the most and not the hydrogen bonding of the solution where the presence of ions doesn't significantly change the hydrogen bonding network[5]. When analyzing the protein/ air and lipid/ air interface, the mechanisms of the Hofmeister anions were mostly related to size[12]. Chaotropes usually have low charge density and are poorly hydrated due to their relatively bigger size and single charge.[25] On the other hand, Kosmotropes usually have high charge density and are well-hydrated due to their relatively smaller size. This suggests that Kosmotropes are able to disrupt the hydrogen bonding of water molecules forming hydration shells around it at the interface[25] while Chaotropes are more easily solvated within the water bulk than the Kosmotropes.[26] This is why as we go from left to right (from Kosmotropes to Chaotropes) in Figure 1, the surface tension increments decrease.
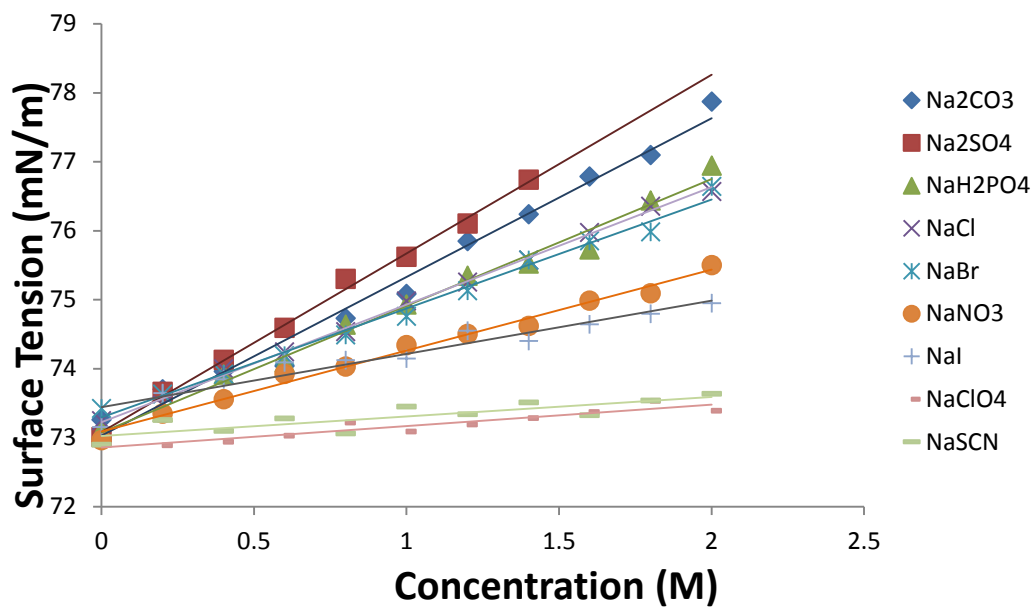
Figure 3. Surface tension of salt solutions as a function of salt concentration.

Table 2. Surface tension increments obtained by Attention Theta optical tensiometer along with the literature values.

Salts	Increments (mN m^{-1}M^{-1})	Literature values[23,24]	Literature values[5]
Na_2CO_3	2.30	*	2.6
Na_2SO_4	2.59	2.77 ± 0.09	2.7
NaH_2PO_4	1.84	*	2.3
NaCl	1.70	1.73 ± 0.17	1.6
NaBr	1.58	1.47 ± 0.21	1.3
$NaNO_3$	1.17	1.23 ± 0.02	1.1
NaI	0.77	1.14 ± 0.09	1.0
$NaClO_4$	0.31	*	1.4
NaSCN	0.28	*	0.5

Table 3. Different physical characteristics of Hofmeister anions. Values obtained from "ion properties" authored by Yizhak Marcus.[28]

Anions	V_i^o	Polarizability	$\Delta_{hydr} S^o$	$\Delta_{hydr} H^o$	$\Delta_{hydr} G^o$
CO_3^{2-}	6.7	4.539	-245	-1397	-479
SO_4^{2-}	25	5.466	-200	-1035	-1090
$S_2O_3^{2-}$	38.2	9.196	-180	*	*
$H_2PO_4^-$	34.6	5.787	-166	-522	-473
F^-	4.3	0.876	-137	-510	-472
Cl^-	23.3	3.421	-75	-367	-347
Br^-	30.2	4.852	-59	-336	-321
NO_3^-	34.5	4.134	-76	-312	-306
I^-	41.7	7.512	-36	-291	-283
ClO_4^-	49.6	5.062	-57	-246	-214
SCN^-	41.2	6.739	-66	-311	-287

Effects of Amino Acids on Surface Tension of Water at Different pH Values

The amino acids used in this study were glycine, L-alanine, and L-serine. Their chemical structures are shown in Figure 4. The pK_a values for the carboxyl and amino groups of these amino acids are listed in Table 4.[29] The presence of protonated or deprotonated species of these amino acids is dependent on the pH of the solution. If the pH of the solution is less than the pK_a, protonated species of amine and carboxyl groups dominate and when pH of the solution is greater than the pK_a, deprotonated species are dominant. By analyzing the behavior of each amino acid individually and comparing it to other amino acids with different R groups, we are able to make predictions on how the functional groups, the amine and carboxyl groups, and the side chain affect the surface tension of water. The percent of the different species in an amino acid solution can be calculated using the Henderson-Hasselbalch equation:

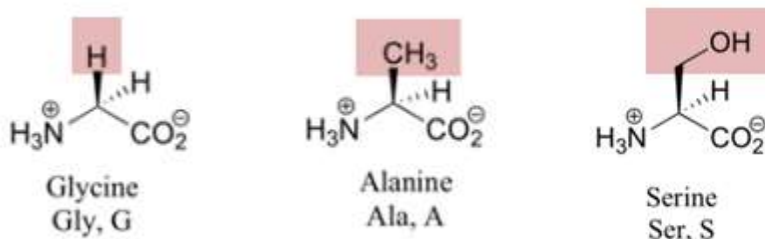$$pH = pK_a + \log([A^-]/[HA]) \qquad\qquad \text{eq. 4.}$$

Figure 4. Chemical structures of glycine, alanine, and serine. The side chains are highlighted as pink. The structures are taken from the website: aquaculture.ugent.be.

Table 4. pK_a of different amino acids used in the experiment.[29]

	Glycine	**Alanine**	**Serine**
Carboxyl	2.35	2.35	2.19
Amino	9.78	9.87	9.21

Table 5. Densities (g/cm^3) of different amino acids collected my Anton Paar DMA 4500 density meter.

Conc. (M)	**Glycine**	**Alanine**	**Serine**
0.2	1.00360	1.00297	1.00610
0.4	1.00981	1.00867	1.01494
0.6	1.01593	1.01431	1.02356
0.8	1.02172	1.01988	1.03210
1.0	1.02763	1.02555	1.04071

Table 6. Surface tension increments of amino acids at different pH solutions.

STI (mN m^{-1}M^{-1})	Glycine	Alanine	Serine
pH 2	0.62	-0.58	1.05
pH 4	1.00	0.81	1.08
pH 7	0.98	1.11	1.20
pH 9		0.63	0.66
pH 11	1.41	-0.65	1.02

Densities of amino acid solutions are obtained at several concentrations as shown in Table 5 before the surface tension measurement. The density measurements were performed before the solution pH was adjusted to the desired pH value. The surface tension of glycine solutions at different concentrations and solution pH are shown in Figure 5. The surface tension increases linearly as a function of glycine solution at all of the pH values studied. The data are fitted with eq. 3 to obtain the surface tension increments at different pH values. The results are shown in Table 6. The percent composition of different groups of glycine is calculated by using Henderson-Hasselbalch equation, eq. 4, as displayed in Table 7. The surface tension increment at pH 11 is the highest of value +1.41. This suggests that the deprotonated carboxyl group contributes the most to the increase of surface tension. When both protonated amine and deprotonated carboxyl groups are present, the surface tension increment decreases to +1.00 for pH 4 and +0.98 for pH 7. This decrease might be an indication that the presence of both positive and negative charged ions slightly cancels each other effect. At pH 2, the surface tension increment decreases the least (+0.62). This decrease might be due to abundance of the protonated carboxyl group.
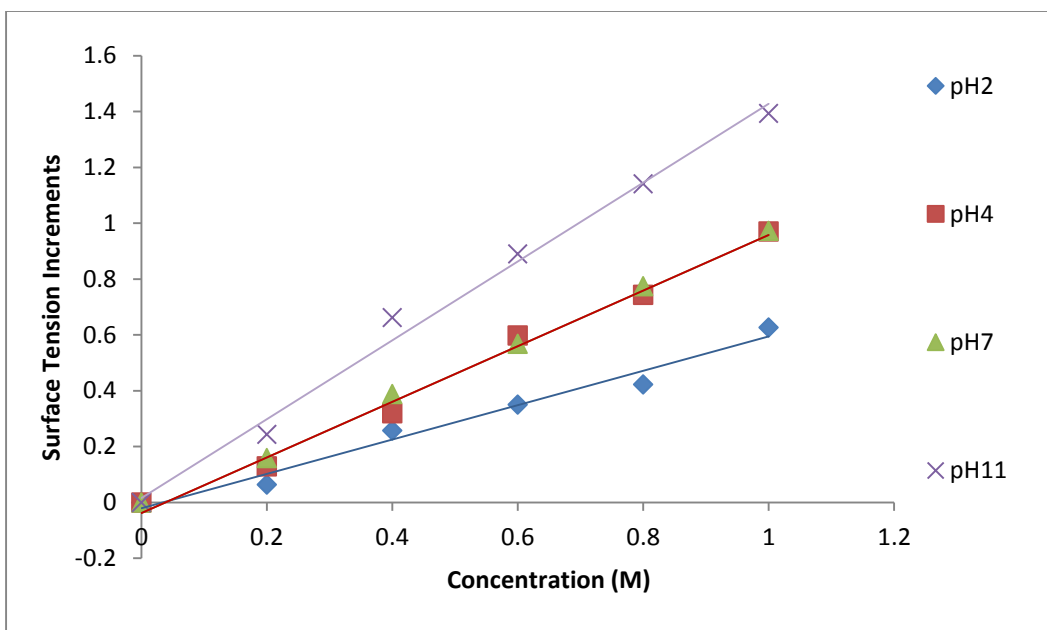
Figure 5. Surface tension increments of glycine solutions as a function of concentration at different pH values.

Table 7. Percent composition of different groups of glycine according to Henderson-Hasselbalch equation.

pH	[NH$_3^+$]	[NH$_2$]	[COOH]	[COO$^-$]
2	~ 100%	~ 0%	69%	31%
4	~ 100%	~ 0%	2%	98%
7	~100%	~ 0%	~ 0%	~ 100%
11	6%	94%	~ 0%	~ 100%

While all the slopes are positive for glycine at different pH values, this is not the case for alanine (Figure 6). The calculations of the percent composition of the functional groups in alanine are listed in Table 8. At pH 7, where both amine and carboxyl ions dominate, a positive surface tension increment was observed (+1.11). As one of the ions decreases, the slope decreases accordingly. At pH 4, the slope decreases to 0.81, and at pH 9, the slope decreases to

0.63. However, when one of the ions dominates, a negative surface tension increment is observed. At pH 2, where protonated amine group mostly dominates, we observe an increment of -0.58 and at pH 11, where deprotonated carboxyl group mostly dominates, we observe an increment of -0.65. Such a phenomenon might be due to the presence of the hydrophobic R group (methyl group in case of alanine) which would most likely contribute to the overall decrease of the surface tension when one of the ions is only present.
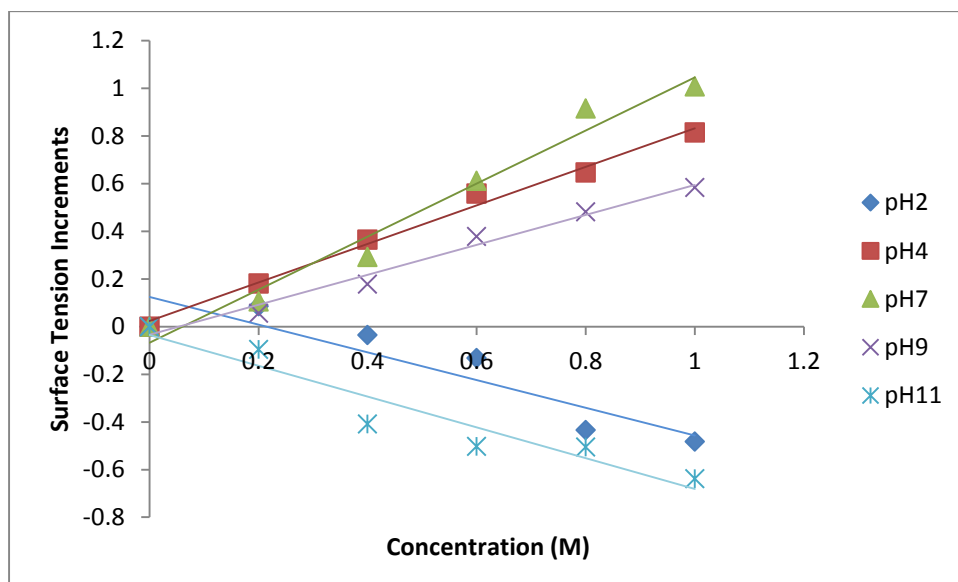

Figure 6. Surface tension increments of alanine as a function of concentration at different pH values.

Table 8. Percent composition of different groups of alanine according to Henderson-Hasselbalch equation.

pH	[NH_3^+]	[NH_2]	[COOH]	[COO^-]
2	~100%	~0%	69%	31%
4	~100%	~0%	2%	98%
7	~100%	~0%	~0%	~100%
9	88%	12%	~0%	~100%
11	7%	93%	~0%	~100%

The experiments with serine show that the increments are all positive as observed in the experiments with glycine. The highest increment (+1.20) was reached when both of the ions dominate. With the exception of pH 9, surface tension increments are relatively close to each other. The presence of additional hydroxyl group might be contributing to the stability of the surface tension.
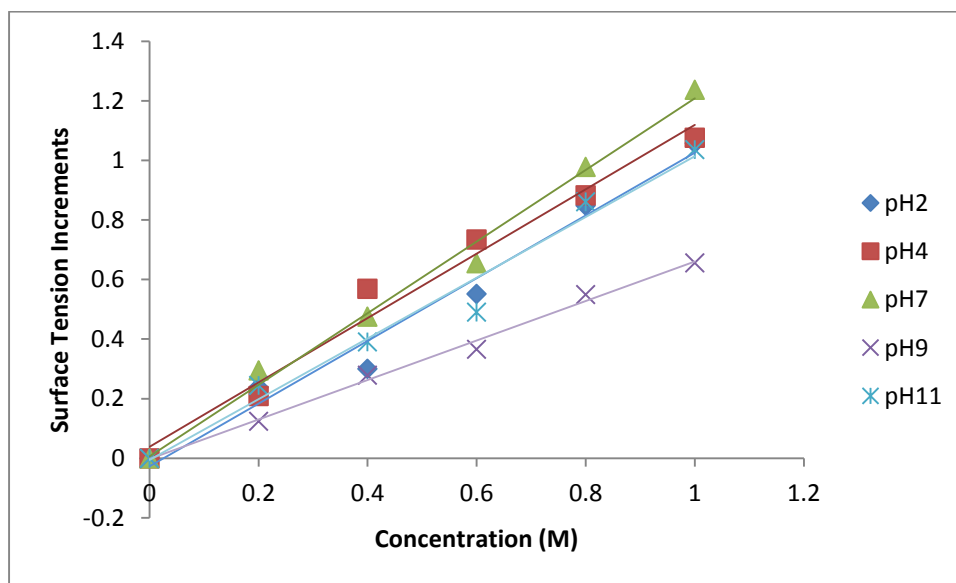

Figure 7. Surface tension increments of serine as a function of concentration at different pH values.

Table 9. Percent composition of different groups of serine according to Henderson-Hasselbalch equation.

pH	$[NH_3^+]$	$[NH_2]$	[COOH]	$[COO^-]$
2	~ 100%	~ 0%	61%	39%
4	~ 100%	~ 0%	2%	98%
7	99%	1%	~ 0%	~ 100%
9	62%	38%	~0%	~100%
11	2%	98%	~ 0%	~ 100%

Our model system is simplified and limited to studying the behavior of individual amino acids and their side chains on surface tension of water. There have been studies done related to this, but on a more complex level where amino acids are analyzed within more sophisticated molecules like surfactants. Previous studies has shown that the pK_a of the amine group of the amino acid decreases at the surface comparing to the bulk[30] while that of carboxyl group increases[31]. This suggests that the water surface is mostly populated with neutral species as compared to the bulk. Elizabeth C. Griffith and her group used infrared reflection-absorption spectroscopy (IRRAS) in order to compare the ionization state of L-phenylalanine at the surface and the bulk of the aqueous solution[32]. Griffith suggests that the change in surface tension is due to the ionization state of the carboxyl and amine group which is proven to be different from that of the bulk. It is suggested by Griffith that the polar groups at the interface only exhibit a decrease in pK_a as compared to the bulk. Most researchers acknowledge that there is a shift in the pK_a of molecules at the surface, yet there is still no agreement on the direction or magnitude of this shift. [32]Amalie and her group came to a conclusion that at lysine's natural pH (around 4) and pH 9, the change of surface tension can be attributed to the neutral species (amine group) while that at very low pH (2) it is due to the ions when studying the self-assembly pH-sensitive cationic lysine based surfactants.[33] It is concluded that the neutral species cause the decrease of

surface tension due to their adsorption to the surface where adsorption can be calculated according to the following equation[33]:

$$\Gamma = -\frac{1}{nRT}\frac{d\gamma}{d\ln C} \qquad \text{eq. 5}$$

where Γ is the adsorption, R is the gas constant, T absolute temperature, γ surface tension, C concentration, and n the number of free species per surfactant molecule. This means that the less neutral species we have in a particular solution, the higher the surface tension. Comparing our results with the literature, we may raise a question whether the percentage calculated according to Henderson-Hasselbalch equation is a suitable method to understand the mechanisms of the amino acids at the surface at different pH values.

Conclusion

The mechanisms of the amino, carboxyl and R groups of different amino acids at different pH solutions are still not fully understood. From our experimental results and calculations, we predict that the surface tension increases due to the abundance of ionic species as compared to the neutral and the hydrophobic groups. On the other hand, some literature shows that the distribution of the ionic and neutral species is not the same when comparing the bulk. This discrepancy raises questions concerning our calculations and the actual reason behind the changes occurring to the surface tension of water.

Future work

We would like to continue measuring the surface tension at the aqueous/ hydrophobic interface after some modifications to our initial experimental approach the setup conditions that are preventing us from taking the measurements. Also, we would like to study other amino acids and their interaction with water at different pH values including phenylalanine, tyrosine, valine, lysine and arginine.

References

(1) Kunz, W.; Henle, J.; Ninham, B.W. "ZurLahre Von Der Wirkung Der Salze (About the science of the effect of salts): Franz Hofmeister's historical papers" *Current Opinion in Colloid & Interface Science* 2004, *9*, 19-37.

(2) Abernethy, J. L., *J. Chem. Ed.*, 1967, 44, 177-180

(3) Zhang, Y.J.; Cremer, P.S. "Interactions between macromolecules and ion: Hofmeister effects" *Current Opinion in Chemical Biology* 2006, *10*, 658-663.

(4) Zhang, Y.J.; Cremer, P.S. "The inverse and direct Hofmeister for lysozyme" *Proceedings of the National Academy of Sciences of the United States of America* 2009, *106*, 15249-15253.

(5) Zhang, Y.J.; Furyk, S.; Bergbreiter, D.E.; Cremer, P.S. "Specific ion effects on the water solubility of macromolecules: PNIPAM and the Hofmeister series". *J. Am. Chem. Soc.* 2005, *127*, 14505-14510.

(6) Gurau, M. C., Lim, S., Castellana, E. T., Albertoria, F., Kataoka, S., Cremer, P.S., *J. Am. Chem. Soc.*, 2004, 126, 10522-10523

(7) Y. Zhang, P.S. Cremer, Chemistry of Hofmeister anions and osmolytes, *Annu. Rev. Phys. Chem.* 61 (2010) 63–83.

(8) Baldwin, R. L. How Hofmeister ion interactions affect protein stability. *Biophys. J.* 1996, *71*, 2056-2063.

(9) Arakawa, T.; Timasheff, S. N. "Mechanism of protein salting in and salting out by divalent cation salts: Balance between hydration and salt binding". *Biochemistry (N. Y.)* 1984, *23*, 5912-5923.

(10) Arakawa, T.; Timasheff, S. N. Preferential interactions of proteins with salts in concentrated solutions. *Biochemistry (N. Y.)* 1982, *21*, 6545-6552.

(11)   Metrick, M. A.; MacDonald, G. Hofmeister ion effects on the solvation and thermal stability of model proteins lysozyme and myoglobin. *Colloids Surf. A Physicochem. Eng. Asp.* 2015*, 469*, 242-251.

(12)   Omta, A. W.; Kropman, M. F.; Woutersen, S.; Bakker, H. J. Negligible effect of ions on the hydrogen-bond structure in liquid water. *Science* 2003, 301, 347-349.

(13)   Schwierz, N.; Horinek, D.; Netz, R. R. Specific ion binding to carboxylic surface groups and the pH dependence of the 26ehavior26r series. *Langmuir* 2015*, 31*, 215-225.

(14)   Kalra, A., Tugcu, N., Cramer S. M., Garde, S., *J. Phys. Chem. B*, 2001, 105, 6380-6386.

(15)   Omta, A. W.; Kropman, M. F.; Woutersen, S.; Bakker, H. J. Negligible effect of ions on the hydrogen-bond structure in liquid water. *Science* 2003, 301, 347-349.

(16)   Mancinelli, R.; Botti, A.; Bruni, F.; Ricci, M. A.; Soper, A. K. Hydration of sodium, potassium, and chloride ions in solution and the concept of structure maker/breaker. *J. Phys. Chem. B* 2007, 111, 13570-13577.

(17)   Yang, Q.; Zhao, J. Hofmeister effect on the interfacial dynamics of single polymer molecules. *Langmuir* 2011*, 27*, 11757-11760.

(18)   Nelson, N.; Schwartz, D. K. Specific ion (Hofmeister) effects on adsorption, desorption, and diffusion at the solid-aqueous interface. *J. Phys. Chem. Lett.*2013*, 4*, 4064-4068.

(19)   Sachs, J. N.; Woolf, T. B. Understanding the Hofmeister effect in interactions between chaotropic anions and lipid bilayers: Molecular dynamics simulations. *J. Am. Chem. Soc.* 2003*, 125*, 8742-8743.

(20)   Brown, E. C.; Mucha, M.; Jungwirth, P.; Tobias, D. J. Structure and vibrational spectroscopy of salt water/air interfaces: Predictions from classical molecular dynamics simulations. *J. Phys. Chem. B* 2005*, 109*, 7934-7940.

(21)   Pegram, L. M.; Record Jr., M. T. Hofmeister salt effects on surface tension arise from

partitioning of anions and cations between bulk water and the air-water interface. *J. Phys.*

Chem. B 2007*, 111*, 5411-5417.

(22)   Haldar, S.; Maji, S. K. Role of non-covalent interactions in the molecular organization of

N-n-hexadecanoyl amino acid amphiphiles with hydrophobic Ca-side chains in Tris buffer

(pH 9.3). *Colloids Surf. A Physicochem. Eng. Asp.* 2013*, 420*, 10-21.

(23)   Chang, Y.; Lin, S. -. Surface tension measurement of glass melts using sessile or pendant

drop methods. *J. Taiwan Inst. Chem. Eng.* 2011*, 42*, 922-928.

(24)   Pegram, L. M.; Record Jr., M. T. Partitioning of atmospherically relevant ions between

bulk water and the water/vapor interface. *Proc. Natl. Acad. Sci. U. S. A.* 2006*, 103*, 14278-

14281.

(25)   Nucci, N. V.; Vanderkooi, J. M. Effects of salts of the Hofmeister series on the hydrogen

bond network of water. *J. Mol. Liq.* 2008*, 143*, 160-170.

(26)   López-León, T.; Santander-Ortega, M. J.; Ortega-Vinuesa, J. L.; Bastos-González, D.

Hofmeister effects in colloidal systems: Influence of the surface nature. *J. Phys. Chem.*

C 2008*, 112*, 16060-16069.

(27)   Pegram, L. M.; Record Jr., M. T. Thermodynamic origin of hofmeister ion effects. *J.*

Phys. Chem. B 2008*, 112*, 9428-9436.

(28)   Marcus, Yizhak. Ion Properties. New York: Marcel Dekker, 1997. Print.

(29)   Website: academics.keene.edu/rblatchly/Chem220/hand/npaa/aawpka.htm

(30)   Ariga, K.; Nakanishi, T.; Hill, J. P.; Shirai, M.; Okuno, M.; Abe, T.; Kikuchi, J. -.

Tunable pK of amino acid residues at the air-water interface gives an L-zyme (Langmuir

Enzyme). *J. Am. Chem. Soc.* 2005*, 127*, 12074-12080.

(31)   Tang, C. Y.; Huang, Z.; Allen, H. C. Binding of Mg^{2+} and Ca^{2+} to palmitic acid and deprotonation of the cooh headgroup studied by vibrational sum frequency generation spectroscopy. *J. Phys. Chem. B* 2010*, 114*, 17068-17076.

(32)   Griffith, E. C.; Vaida, V. Ionization state of l -phenylalanine at the air-water interface. *J. Am. Chem. Soc.* 2013*, 135*, 710-716.

(33)   Mezei, A.; Pérez, L.; Pinazo, A.; Comelles, F.; Infante, M. R.; Pons, R. Self assembly of pH-sensitive cationic lysine based surfactants. *Langmuir* 2012*, 28*, 16761-16771.