Ionizing Surface Potential Measurements of Electrolyte Solution Surfaces

Dissertation

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science

in the Graduate School of The Ohio State University

By

James Dohrman

Graduate Program in Chemistry

The Ohio State University

2023

Master's Examination Committee:

Dr. Heather C. Allen (Advisor)

Dr. John Herbert

Copyrighted by

James Dohrman

2023

Abstract

The surface of a solution exhibits a number of chemically unique properties compared to the bulk that are of extreme interest. Several metrics to examine the surface exist, including examining the electrical nature of the boundary. One method of examining this is the ionizing surface potential method, which allows for measuring the potential across the surface layer of a solution.

This work examines experiments using an ionizing surface potential sensor (ISPS) which was fabricated by Dr. Tehseen Adel with several improvements over older models, such as the use of an Am-241 electrode instead of a Po-210 electrode. The method of data collection, its accuracy, and the trends that can be found among the resulting data will be examined and explained in detail in order to consolidate the necessary information for the understanding and operation of this instrument. Data was taken of previously examined compounds to use as points of comparison along with some unexamined compounds that can be compared to previously existing trends.

| 2021 | |
|-----------|---|
| | |
| | |
| 2021-2022 | |
| | Department of Chemistry and Biochemistry, The Ohio State University |

Major Field: Chemistry

Vita

Table of Contents

| Abstract | ii |
|-----------------|-----|
| Vita | iii |
| List of Figures | v |
| Introduction | 1 |
| Experiments | 4 |
| Results | |
| Conclusion | |
| Bibliography | 11 |

List of Figures

- Figure 1 Diagram of the sample cell. V_m is the measured potential difference. Page 9.
- Figure 2 Displayed output of a single measurement of surface potential over time for H₂O. Page 10.
- Figure 3 Comparison of change in surface potential between various sodium-halide salts. Page 11.
- Figure 4 Comparison of surface potential data of MgCl₂ to control samples. Page 13.
- Figure 5 Comparison of surface potential data of MgCl2 to control samples. Does not use the surface potential values calculated relative to water, or $\Delta \chi$, but water is included for comparison. Page 13.

Chapter 1. Introduction

The goal of this thesis is to gain understanding of the general principles behind surface potential measurement, including variations in electric fields near the solution surface and the causes behind these variations. Additionally, the ionizing surface potential sensor (ISPS) which was used to collect the surface potential data presented here will be examined. Combining the understanding of these two topics will allow for the interpretation of the surface potential data obtained through the ISPS and the trends present among the results.

Background

Gas-Liquid interface

The gas-liquid interface is a region that exhibits different properties than either the bulk liquid or gas phases due to interactions between the two. The attractive forces between the molecules of the liquid cause an inward force towards the bulk as there are no neighboring molecules of the same type to be strongly attracted to on the gaseous side of the interface. This force is the surface tension, which restrains the liquid from crossing the interface freely.

The forces involved in causing the surface tension also affect the arrangement of molecules at the surface. For instance, in aqueous solutions, the water molecules tend to be oriented with an O-H group pointing towards the air at the surface, with the layer immediately below the surface having an O-H group point down into the water. These different arrangements lead to some ions being attracted to the interface and others being largely contained in the bulk. In the order of the Hofmeister series, $F^- \approx SO_4^{2-} > CI^- > NO_3^- > Br^- > I^- > SCN^-$, ions to the left tend to increase the surface tension of water and are excluded from the surface, whereas the ions to the right cause the surface tension of water to be comparatively lower and are attracted to the interface. The rightmost ions of the series even tend to adsorb to the surface.¹ Due to the presence of molecules able to interact with the interface from the gas phase and ions

adsorbed to the surface from the bulk; there are also particular surface sensitive reactions that take place at interfaces.

Surface Electrical Potential

The surface electrical potential is defined as the potential difference between molecules at the surface and molecules in the bulk. The surface potential of aqueous solutions is dependent on the electromagnetic interactions at the surface and is tied to the arrangement of water molecules, ion adsorption or desorption, and the presence of ion-water structures.² Information about these properties can therefore be determined from the surface potential, as well as information about properties directly affected by the surface potential such as the surface tension, which in general decreases with increasing surface potential. Notably the surface potential measurement does not include the potential difference between the air and the interface, which can make it difficult to determine. However, several measurement techniques exist that can allow the surface potential to be measured without interference from the air, including the vibrating plate method, the liquid flow method, and the ionizing surface potential method. Of these, the ionizing surface potential method was used.

Ionizing Surface Potential Method

In order to measure the surface potential, the resistance between the measuring electrodes must be lower than the resistance over the entire measuring circuit. Ionizing the air by exposing it to alpha particles from a radioactive electrode decreases the resistance of the air, negating the potential difference between the air and the interface and allowing for the direct measurement of the potential difference.³

When the method was developed, polonium-210 was used as the material for the electrode, but the instrument used to collect the data for this thesis uses an americium-241 electrode, which is cheaper, easier to acquire, and has a longer half-life meaning it can go longer without replacement.

There are a variety of potential sources of error that can be introduced to the sample cell that have been controlled for. Controlling the distance between the Americium electrode and the platinum gauze counter electrode allows for preventing the ionization of the liquid surface. Encasing the sample chamber in PTFE and purging with nitrogen provides electrical insulation and prevents contamination.

Chapter 2. Experiments

The ionizing surface potential sample cell is a PTFE (Teflon) dish with a lid. An Am-241 electrode is suspended above the sample cell in the lid. A platinum gauze counter electrode, which was cleaned by electrically cycling in a 0.1M perchloric acid solution, was placed inside the sample cell and submerged in the sample solution. The sample cell chamber is continually flushed with nitrogen gas while data is being collected.



Figure 1. Diagram of the sample cell. V_m is the measured potential difference.

Once the solution is placed in ionizing cell, the potential of the system is measured for 5 minutes, with one data point taken each second. Water data was taken separately for reference and cetlytrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) data were also taken for reference on samples not being used for data validation.

Graphs of the measured surface potential data plotted against experimental time tend to take the following form:



Figure 2. Displayed output of a single measurement of surface potential over time for H₂O.

The measured surface potential for a given trial is the average of the last 50 seconds of data collection.

Validation of Data, or Sodium Salts Potential Discussion:

Measured surface potential difference $(\Delta \chi)$ is the primary point of comparison between different solution samples and is calculated as $\chi_{solution}$ - χ_{water} , where χ refers to the surface electric potential difference, or the average potential value found for the solution in a single trial. This is done by measuring the surface potential of water across three trials on the same day as the solution surface potential is measured, then subtracting the measured surface potential of water from that of the solution.



Figure 3. Comparison of change in surface potential between various sodium-halide salts.

Even with some data distortion, the expected trend of increasing measured surface potential difference while moving down the halogen column of the periodic table due to increasing particle size and polarizability can be seen.

The expected ranges for the below samples were found by calculating $\Delta \chi$ based on the expected $\chi_{solution}$ and the recorded χ_{water} for the experiment.

CTAB

Samples of CTAB with a concentration of about 0.35mM returned measured surface potential difference values in the expected range of 0.68 V \pm 0.09.⁶

SDS

Samples of SDS with a concentration of about 0.35mM mostly returned measured surface potential difference values in the expected range of -0.16 V \pm 0.06.⁶ Some outliers were found with potential differences slightly higher around 0V.

NaCl

Samples of NaCl with a concentration of about 1M returned measured surface potential difference values in the range of 0.09 V \pm 0.01 instead of the expected range of 0.27 V \pm 0.01.⁶

Na_2SO_4

Samples of Na₂SO₄ with a concentration of about 1M returned measured surface potential difference values in the expected range of $0.04 \text{ V} \pm 0.02$.⁷ Some outliers were found with potential differences that were significantly higher, around $0.32 \text{ V} \pm 0.01$ and $0.19 \text{ V} \pm 0.01$. These were found as a result of improper purification techniques, the values in the expected range resulted from proper purification.

NaBr

Samples of NaBr with a concentration of about 1M returned measured surface potential values in the range of 0.18 V \pm 0.02 when the target range is slightly higher at 0.3 V \pm 0.02.⁶ These samples may have been improperly purified and should be further validated.

NaI

Samples of NaI with a concentration of about 1M returned measured surface potential difference values in the expected range of 0.51 V \pm 0.01.⁶

Chapter 3. Results and Discussion



Figure 4. Comparison of surface potential data of $MgCl_2$ to control samples.



Figure 5. Comparison of surface potential data of MgCl₂ to control samples. Does not use the surface potential values calculated relative to water, or $\Delta \chi$, but water is included for comparison.

Surface potential measurements relative to H₂O, SDS, CTAB, and MgCl₂ are displayed in Figure 4, with the concentration of MgCl₂ being about 1M. The same measurements are displayed as absolute values in Figure 5. H₂O, SDS, and CTAB were used as reference samples to compare to the MgCl₂. Using these as reference, MgCl₂ can also be compared to NaCl, another compound with the Cl⁻ anion. Notably, the data displayed shows the difference between the SDS and MgCl₂ to be smaller than between SDS and NaCl, indicating MgCl₂ has a smaller surface potential difference than NaCl, but with relatively close values of MgCl₂ and NaCl. This somewhat disagrees with expectations, as the doubled concentration of Cl⁻ anions and the presence of a different cation for MgCl₂ should have resulted in a somewhat different surface potential difference by the discrepancy of the NaCl surface potential difference with its expected values, meaning it can most likely be resolved with additional experiments validating the recorded data.

Further evaluation of the absolute potentials displayed in figure 5 also highlights the interesting fact that CTAB has a naturally positive surface potential in contrast to the surface potentials of H₂O, SDS, and MgCl₂. This indicates that the net dipole of the interface is similar to water in SDS and MgCl₂ but reversed in CTAB. The negative potential implies that, on average, the O-H dipole in neat water points the hydrogen into the bulk solution, which means that in the case of MgCl₂ the chloride ions may be more surface active than the magnesium ions, as the negative charge of the chloride ions causing the O-H dipole to point the hydrogen into the bulk can explain why MgCl₂ has a negative surface potential like that of water.

Chapter 4. Conclusion and Future Work

A large amount of the data from validation showed expected results, including the appearance of certain data trends relating to the surface sensitivity of compounds. Some data, particularly that of MgCl₂, should be retaken to further validate accuracy. However, the examination of the surface potential values found with the ISPS and the trends present, including the possibly erroneous exceptions to the trends, demonstrate the general principles of surface potential measurement effectively along with what can be inferred from these results.

In addition to data validation, a trend was observed among the sodium salts where the order of increasing surface potentials among salts followed the Hofmeister series as the anion was changed. Attempting to verify this trend more thoroughly and test it on other salts with different cations is also a promising direction for future research.

Bibliography

1: Collins, K. D.; Washabaugh, M. W. The Hofmeister Effect and the Behaviour of Water at Interfaces. Q. Rev. Biophys. 1985, 18 (4), 323–422. https://doi.org/10.1017/S0033583500005369.

2: Mills, I.; Cvitas, T.; Homann, K.; Kallay, N.; Kuchitsu, K. INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY PHYSICAL CHEMISTRY DIVISION

3: Jarvis, N. L.; Scheiman, M. A. Surface Potentials of Aqueous Electrolyte Solutions. J. Phys. Chem. 1968, 72 (1), 74–78. https://doi.org/10.1021/J100847a014.

4: Jungwirth, P.; Tobias, D. J. Molecular Structure of Salt Solutions: A New View of the Interface with Implications for Heterogeneous Atmospheric Chemistry. J. Phys. Chem. B 2001, 105 (43), 10468–10472. https://doi.org/10.1021/jp012750g.

5: Nakahara, H.; Shibata, O.; Moroi, Y. Examination of Surface Adsorption of Cetyltrimethylammonium Bromide and Sodium Dodecyl Sulfate. J. Phys. Chem. B 2011, 115, 9077–9086.

6: Adel, T.; Ng, K. C.; Vazquez de Vasquez, M. G.; Velez-Alvarez, J.; Allen, H. C.; Langmuir, 2021, 37, 7863–7874. "Insight into the Ionizing Surface Potential Method and Aqueous Sodium Halide Surfaces" (Invited Feature Article).

7: Adel, T.; Velez-Alvarez, J.; Co, A. C.; Allen, H.C.; J. Electrochem. Soc., 2021, 168, 016507. "Circuit Analysis of Ionizing Surface Potential Measurements of Electrolyte Solutions."

8: Adel, T.; Inherent Electric Field Measurements of Liquid Surfaces Using Ionizing Surface Potential,2021.

11