Effect of Pre-Heating on the Surface Tension of NaCl Solutions

Muneer El-Entesh
University of Hebron, muneern@hebron.edu

Follow this and additional works at: https://digitalcommons.aaru.edu.jo/hujr_a

Part of the Life Sciences Commons

Recommended Citation
Available at: https://digitalcommons.aaru.edu.jo/hujr_a/vol7/iss1/4

This Article is brought to you for free and open access by Arab Journals Platform. It has been accepted for inclusion in Hebron University Research Journal-A (Natural Sciences) by an authorized editor. The journal is hosted on Digital Commons, an Elsevier platform. For more information, please contact rakan@aaru.edu.jo, marah@aaru.edu.jo, dr_ahmad@aaru.edu.jo.
Effect of Pre-Heating on the Surface Tension of NaCl Solutions

Dr. Muneer A. F. Natsheh
Department of Chemistry, College of Science and Technology, Hebron University

Abstract:
Surface tension of aqueous sodium chloride solutions has been measured in the concentration range $0 \text{M} \leq C_{\text{NaCl}} \leq 3 \text{M}$ by the Du Nouy ring method. The surface tension of the NaCl solutions increases linearly with increasing salt concentration in good agreement with reported results. Without pre-heating- the NaCl solid sample to 520 $^\circ$C- the surface tension displays a time dependent at a concentration of the 3 M. With pre-heating- the sample at the mentioned temperature- the surface tension stays constant with time due to removal of impurities. This simple experiment indicates the importance of heating in the measurement of surface tension of salt solutions.

Key Words: Surface tension, sodium chloride solutions
Introduction

Liquids with low surface tensions (20 \( \sigma \) 30 mN/m) are almost insensitive to impurities. Because of the fact that the surface tension of the pure liquid is small, impurities of surfactant nature cannot lower significantly that tension. However, impurities can affect noticeably the behavior of capillary systems with high surface tensions. For example, they can cause Marangoni convection due to the gradients of surface tension over the interface. This phenomenon is particularly important in experiments with air-water interfaces (Herrada & Montanero, 2011).

For pure liquids, it is interesting to know how this property will change when a solution is added. Changes of this property will depend on the nature and amount of the solution added. It can either be decreased or increased according to the Gibbs adsorption equation (Atkins & Paula, 2006). Solutes which decrease the surface tension, e.g. water, will have a positive surface excess concentration; this means that the number of solute particles will be higher at the top most surface layer in comparison with the subsequent layers. An example of this type of solutes is surfactant molecules (Duckhin & et al, 1995). Inorganic salts, on the other hand, have been shown to increase the surface tension of water (Randles, Delahay & Tobis 1963; Weissenborn & Pugh, 1996). In this case, the surface excess concentration will be negative which implies that the top most layer is depleted from salt ions, or simply the number of ions present in the surface layer is less than in the subsequent layers (bulk).

Understanding the surface and interfacial behavior is necessary for numerous applications. To mention a few applications among others: thin film coating technology (Schlick, 1996 & Gebelein, 1991) colloid stabilization (Pincus, 1991 & Decher, 1997). The surface tension of aqueous electrolytes solutions have been studied recently both theoretically (Leroy, et al, 2010, Santos, et al, 2012), and experimentally (Matubayasi, etal 1999, 2006, 2007, & Ali et al, 2008). These studies confirmed the increase of surface tension of water by the addition of salt; this behavior is attributed to a combination of factors, namely electrostatic forces, ionic hydration, and dispersion forces. The electrostatic forces depend on the size and charge density of the ions. Ozdemir, et al, (2009) studied the surface tension of chloride salts of sodium and potassium. For both NaCl and KCl, increases of the surface tension of water with
Increasing salt concentration are observed. The increase for NaCl is more pronounced than that of the KCl.

None of these studies have reported clearly on the importance of pre-heating the solid salt before preparing the aqueous solutions. In this short report we demonstrate that without pre-heating, the surface tension would display a time dependent behavior at high molarity. It is always mentioned in these reports that a freshly prepared solution was used, which is of course the right thing to do. The findings here indicate the complex behavior of the surface tension of concentrated salt aqueous solutions and the need for careful sample preparation and removal of impurities which can be only removed at high temperatures. A careful control of that influence can be crucial in many applications of fluid mechanics. For this purpose, an accurate knowledge of the surface tension value over time is crucial to analyze properly the experimental results.

**Experiment**

Sodium chloride salt (Sigma Aldrich) was of reagent grade and used with and without pre-heating to 520 °C. Distilled water was used for the preparation of the salt solutions with a conductivity of 5 µS/cm. All glassware were carefully cleaned. Surface tension was measured with the state-of-the-art K11 MK3 tensiometer (Krüss, Germany). The tensiometer is fully automatic with high resolution (0.01 mN/m) and the constant position force measurement with overload protection. It is equipped with a high precision force sensor that does not have to be recalibrated. All measurements were conducted with the tensiometer chamber closed.

1. The surface tension of pure distilled water was measured, both by the Wilhelmy plate (platinum) and Du Noüy ring (platinum-iridium) methods, several times before and during each measurement to ensure a contamination-free setup.
2. Before each measurement, the plate or the ring was rinsed thoroughly with distilled water and flame-annealed to redness.
3. Values of 72.21 mN/m were obtained by the plate method and 72.15 mN/m by the ring method. These values are in agreement with reported values ranging from 72.0 - 72.7. (Ozdemir & et al,

4. The plate method was used first as it is a correction free method, second because the plate is not moved while surface tension is being measured, and finally the measurement is faster in comparison to the ring method. Each data point is an average of ten measurements with a standard deviation ranging from 0.02 - 0.08 mN/m.

5. All measurements were conducted at room temperature (~ 23 °C). NaCl solutions were prepared by two different methods: one was by successive dilution from the most concentrated one (3 M), and the other by taking the right mass to obtain the desired concentration for each solution. In the former case, the most concentrated solution was stirred by a new magnetic stirrer for enough time until the solution became very clear. In the latter case, the salt was dissolved by rigorous shaking until the salt crystals disappear.

6. One set of measurement was conducted with heating the solid NaCl to 520 °C, while the other set was without heating the solid salt. The time dependent measurements were conducted three times and the results showed good reproducibility.

Results and discussion

Fig. 1 shows the measured equilibrium surface tensions of NaCl aqueous solutions without pre-heating with 0 M ≤ C_{NaCl} ≤ 3 M. Solid circles are the measured points and the solid line is a least square linear fit to the experimental data. Our data are in good agreement with the data of Matubayasi et al (Matubayasi, et al, 1999), and with recently reported data of Ozdemir et al (Ozdemir, et al, 2009). As can be seen, the surface tension of pure water increases linearly with an increase in NaCl concentration. Increasing the surface tension in this case is correlated with the structure of the surface region. An ion free layer and the thickness of the surface region have been correlated to this increase by a treatment based on the Gibbs adsorption equation and thermodynamics. According to the Gibbs adsorption equation, any solute that increases the surface
tension of pure water poses a negative adsorption. This microscopically means that the number of salt ions at the top most surface layer is less than at the subsequent layers (bulk). Though in agreement with experimental findings up to 1 M salt solutions, the classical ideas of Langmuir, Wagner, Onsager and Samaras were that of a strong dielectric discontinuity between air and water results in induced surface charge at the air/water interface. This surface charge produces exactly the same electric field in water as an image charge placed across the dielectric interface. Ion depletion near the Gibbs dividing surface is a consequence of the electrostatic repulsion of ions from their images (Santos, et al, 2012).

![Figure 1](image.png)

**Figure 1.** Concentration dependence of the surface tension of aqueous NaCl solutions at room temperature with pre-heating. The solid circles are experimental data. The solid line is a linear least square fit to experimental points.

Fig. 2 shows the time dependence of the surface tensions of 0.375 M (solid triangles), 1 M (solid stars) and 3 M (solid squares) NaCl (without pre-heating) as indicated in the figure. The surface tensions of the 0.375 and 1 M NaCl solutions do not change during a two-hour time. The data
points at 120 minutes for these two solutions were obtained after having left the solutions for one hour. The mentioning of ‘stirring for 1 minute’ only applies to the 3 M solution. The vertical dashed line separates the time before and after additional one minute stirring. One can safely say that the effect of increasing the surface tension of pure water by the addition of NaCl is relatively stable and even permanent. However, surprisingly the surface tension of the 3 M solution changes with time (~two hours) by ~17% (~12 mN/m) reaching a minimum value of ~65 mN/m which is below that of pure water. Note that the zero time is the starting time of the measurements after the solution was left covered for about two hours. As briefly mentioned in the experimental section, the 3 M solution was first prepared by adding 35.1 g of NaCl to 200 ml volumetric flask and then water was added to the mark. This is a large amount of salt and needs to be well dissolved. For this purpose, a well cleaned magnetic stirrer was used and the solution was stirred long enough (~one hour) until a very clear solution was obtained. The bottom of the flask was checked for any not dissolved salt crystals. The solutions used to obtain fig. 1 were prepared by successive dilution from this concentrated 3 M one. 100 ml of the latter solution were left covered as the measurements started with the more dilute concentration. When the time had come to measure the surface tension of the 3 M solution a value of 65.89 mN/m was obtained. The same measurement was repeated, with the rinsed, flame-annealed platinum plate, three times and the same value was obtained. We strongly think that this time dependent behavior of the surface tension is correlated with the presence of impurities in the solid salt sample. After this low surface tension value was obtained, measurements continued with time and the results obtained are displayed in fig.2 on the left of the dashed line. The surface tension increases with time and reaches a value close to that of water. After ~60 minutes the 3 M solution was additionally stirred for one minute, left to relax for one minute and a value of 77.50 mN/m was obtained; this is in a very good agreement with reported value (Ozdemir, et al, 2009), for 3 M NaCl. Time measurements after the last additional stirring are displayed to the right of the dashed line of fig. 2. As can be seen in this region of the figure, the surface tension stayed constant for about 30 minutes and then
gradually decreased with time and finally reached a value of ~ 65 mN/m, as that at zero time in fig. 2.

![Graph showing the time-dependence of the surface tension of NaCl solutions](image)

**Figure 2.** Time-dependence of the surface tension of 0.375 M (▲), 1 M (●) and 3 M (■) aqueous NaCl solutions (without pre-heating) at room temperature. The solid lines are drawn to guide the eye. The vertical dashed line separates the region of time-dependent measurements before and after additional stirring for 1 min. Additional stirring applies only to the 3 M solution.

The same whole measurements were repeated two times with solutions prepared not by successive dilution but instead by taking the desired mass of the salt each time to obtain the desired concentration. It’s worth mentioning that a 2 M NaCl solution displayed the same behavior (not shown) as that of the 3 M solution. From our intensive measurements, we can state that below 2 M NaCl solutions the increase of the surface tension of water is time independent while at or above 2 M the effect is time dependent. So the effect of increasing the surface tension of water by the addition of salt at high concentrations is not a permanent effect. All
reports in this particular field of research mentioned that the surface tensions have been measured using freshly prepared salt solutions and do not change significantly with time (see e.g. Matubayasi et al (Matubayasi, et al, 1999) and Ozdemir et al (Ozdemir, et al, 2009). Figure 2 of the work by Ozdemir et al shows that the surface tension does not change with bubble age up to the highest concentration measure of 5.2 M. The upper limit of the time frame used was only 300 seconds (five minutes) here. The effect being discussed here does not even resemble that of surfactant solutions where it is well known that the addition of surfactant decreases the surface tension of water at least until the critical micelle concentration of the surfactant (unclear) but time dependent measurements show a decrease of the surface tension with time. No decreasing or increasing effect of surfactant solution with time has been reported so far. Even the amount of decrease in the case of surfactant is much less than the effect reported here (Santos, et al, 2012). There are reports on the initial decrease and then an increase of the surface tension of some salt solutions using the capillary rise method, the so called Jones-Ray effect. These authors reported in 1941 on a minimum of the surface tension of KCl, CsNO$_3$ and K$_2$SO$_4$ around 1mM concentration. This result (minimum) was confirmed in 2004 by resonance enhanced femtosecond second harmonic generation (Petersen, et al, 2004). However, the effect found here is completely different from the Jones-Ray effect in terms of the concentration of the salt and the detailed behavior of the surface tension with time.

Figure 3 shows the time dependent of the surface tension of 1 M NaCl solution (open circles) and 3 M solution (open square). This figure is important because it demonstrates the important effect of impurities which causes major contamination of surfaces of its solutions if they are strongly adsorbed. The data in figure 2 were obtained without pre-heating the solid salt, and the aqueous salt solution displays a time dependent behavior. The data in figure 3 were obtained with pre-heating the solid salt. One can clearly see that the time dependent behavior of the surface tension has disappeared due to removal of impurities by heating at elevated temperature.
Conclusions
The surface tension of aqueous solutions of NaCl salt has been studied by the Wilhelmy plate method. The static surface tensions of all studied solutions are in good agreement with the reported values. The time dependent measurements showed that at low salt concentration < 2M, the surface tension does not change with time. Above 2M, the surface tension however displayed a considerable change with time is the solid salt is not pre-heated. An example is presented here for the 3M solution where the surface tension changes from 77.47 mN/m to 65.89 mN/m with time. Upon heating the solid salt, the impurities are removed and the time dependent effect is eliminated. This emphasizes the importance of heating of the solid salt at elevated temperature in these types of measurements.

Acknowledgment
We thank Alexander von Humboldt Foundation, Germany, for donating the Krüss K11 MK3 tensiometer which made these measurements possible.
References


Leroy, P; Lassin,, A; Azaroual, M; André,, L. (2010). Geochimica and Cosmochimica Acta 74, 19 , p 5427-5442.


Drellich, J; Fang, Ch; White, C.L, (2002). *Encyclopedia of Surface and Colloid Science*