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Surface Tension of Seawater

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Surface Tension of Seawater

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New measurements and a reference correlation for the surface tension of seawater at atmospheric pressure are presented in this paper. Surface tension of seawater was measured across a salinity range of $20 \leq S \leq 131$ g/kg and a temperature range of $1 \leq t \leq 92$ °C at atmospheric pressure using the Wilhelmy plate method. The uncertainty within measurements varied from 0.18 mN/m to 0.37 mN/m with the average uncertainty being 0.22 mN/m. The experimental procedures were validated with tests conducted on ACS reagent grade water and aqueous sodium chloride solutions. Literature data and present measurements were evaluated and a reference correlation was developed expressing surface tension of seawater as a function of temperature and salinity. The average absolute percentage deviation between measurements and the correlation was 0.19% while the maximum deviation was 0.60%.

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1. INTRODUCTION

The surface tension of seawater is an important thermodynamic property for accurately designing seawater desalination technologies where vapor transfer occurs across a liquid-air or liquid-vapor interface. For example, surface tension plays a key role in tailoring the non-wettability of membranes in membrane distillation[1] and in optimizing heat and mass transfer in packed beds and falling film evaporators for humidification-dehumidification desalination systems[2] and multi-effect distillation[3] respectively. It also affects the thermal performance of seawater cooling towers[4]. While there is data on the surface tension of seawater in the oceanographic range of temperature and salinities ($0 \leq t \leq 40$ °C and $0 \leq S \leq 40$ g/kg) from previous literature[5–7], there is no data in the standard operating range for thermal desalination ($40 \leq t \leq 100$ °C and $40 \leq S \leq 120$ g/kg). In this work, new reference data for the surface tension of seawater across the oceanographic and desalination ranges is presented. A critical evaluation of the past data has been conducted and a reference correlation for the surface tension of seawater is proposed.

Seawater is an aqueous mixture of several electrolytes. While the concentration of the

mixture can vary significantly around the world's oceans - the inorganic chemical composition of the mixture is fairly uniform[8]. This has allowed for the definition of a reference composition of seawater, the concept of "Absolute Salinity" - defined as the "mass fraction of dissolved materials in seawater" and characterizing seawater physical properties as a function of only temperature, pressure and salinity[8]. However, the absolute salinity of seawater is experimentally difficult to determine and can only be approximated using various salinity scales defined in oceanography. Historical scales include "Knudsen Salinity" (S_{K})[9], "Chlorinity" (Cl)[10] and "Practical Salinity" (S_{P})[11]. The present standard used in this work, the "Reference Salinity" scale (S)[8], is the most accurate approximation currently available. The term "salinity" is used subsequently to refer to "Reference Salinity". The detailed descriptions of these as well as equations to convert between each salinity scale can be found in Millero *et al.*[8] Like salinity, different temperature scales have been used historically. A description of the present standard, the ITS-90 temperature scale, used in this work and scales used by previous work such as the ITS-27, IPTS-48 and the IPTS-68 scales are given by Preston-Thomas[12] while conversion tables between these are given by Goldberg *et al.*[13] Literature data reported in historical salinity and temperature scales were converted to the current Reference Salinity scale and ITS-90 temperature scales respectively, and analyzed.

Over the last hundred years, only three major studies measured the surface tension of seawater — by Krummel[5] in 1900, Chen *et al.*[6] in 1994 and Schmidt *et al.*[7] in 2011. Krummel used Jaeger's variant of the bubble pressure method[14] to measure the surface tension of five samples of North Sea seawater with Knudsen salinities S_{K} = (7.73, 13.00, 15.82, 24.96 and 34.90) g/kg at atmospheric pressure and at a fixed temperature of 13.25 ± 0.45 °C. While Krummel did not clearly state the uncertainty in measurements, evaluation of random and systematic errors in the dataset revealed an overall uncertainty of 1.35%. Here, the systemic error was evaluated by comparing Krummel's value for the surface tension of pure water with the International Association for the Properties of Water and Steam (IAPWS) correlation for the surface tension of pure water[15]. Chen *et al.* used the maximum bubble pressure method to measure the surface tension of six samples of North Pacific seawater with practical salinities S_{P} = (4.965, 15.220, 20.006, 25.062, 29.464 and 34.486) at atmospheric pressure over a temperature range of 15 to 35 °C. The original solution used was 0.45 μm microfiltered seawater of salinity S_{P} = 34.486 collected off the coast of Japan. Test solutions of lower salinities were prepared by diluting the original solution with water. The stated accuracy of

the tensiometer was 0.2%. However, the actual uncertainty in measurements may be higher because at each temperature and salinity, surface tension was measured only once.

Organic surface active material present in natural seawater is known to lower it's surface tension[7,16–18]. Studies by Krummel and Chen *et al.* did not take steps to address this concern and thus, trace organic surfactants may have been present in their natural seawater samples. Schmidt *et al.* addressed this concern measuring the surface tension of surfactant-free seawater from the Baltic sea ($S_P = 11.4$) and the Atlantic ocean ($S_P = 35.4$). Seawater samples were made surfactant-free using solid phase extraction. Commercially available cartridges that adsorbed polar and aromatic compounds but not inorganic salts were used for this purpose. Surface tension was measured at atmospheric pressure over a temperature range of 5 to 30 °C using the Wilhelmy plate method. Careful measurements of surface tension were also carried out on deionized water. These measurements were reported to agree within 0.1 mN/m of the international tables for the surface tension of pure water[19].

Correlations for the surface tension of seawater were developed by Krummel, Chen *et al.* and Schmidt *et al.* using their own measurements. Data from these studies were also used by other authors to generate new correlations. In 1939, Fleming and Revelle[20] improved Krummel's correlation using updated measurements of the surface tension of pure water. Sharqawy *et al.*[21] in 2010 used data from the studies of Krummel and Chen *et al.* and normalized them to the IAPWS correlation for the surface tension of pure water.

In this work, new accurate measurements for the surface tension of seawater at atmospheric pressure across a temperature range of $1 \leq t \leq 92$ °C and salinity range of $0 \leq S \leq 131$ g/kg are presented along with the experimental procedure and an uncertainty analysis. Measurements presented here are so far the only reported values for seawater surface tension beyond a temperature of 35 °C and salinity of 35 g/kg. For generating the main reference data, seawater samples were prepared from the ASTM D1141 standard for substitute ocean water[22] (referred hereafter as ASTM seawater). The ASTM seawater standard was preferred over other standards such as the IAPSO standard[8,23] and the OSIL Atlantic Seawater Conductivity Standard (ASCS)[24] because ASTM D1141 seawater is a laboratory preparation devoid of organic content that might otherwise affect the repeatability of surface tension measurements. IAPSO and ASCS seawater by comparison is natural seawater collected from the Atlantic that is microfiltered through a 0.2 μm membrane, treated with ultraviolet radiation and calibrated to a standard salinity. While the organic content in

IAPSO and ASCS seawater is low by virtue of the treatment process, trace concentrations of organic surfactants may still exist. For comparison purposes and to verify whether results from ASTM seawater could be applied to properly treated natural seawater, surface tension measurements of ASCS seawater are also presented. Experimental procedures were validated by measuring the surface tension of ACS reagent grade water and aqueous sodium chloride solutions and comparing these with literature correlations.

For developing and assessing a reference correlation for the surface tension of seawater, primary and secondary experimental data were used. While primary data were used to generate the correlation, secondary data were used for comparing with the correlation. To select primary data, experimental data from literature and from the present work was critically evaluated using some of the criteria laid out in a previous evaluation of surface tension data by Jasper[25] such as: purity of compound, experimental procedure and estimation of reliability. Importance was given to the purity of seawater particularly the absence of organic surfactants in seawater.

2. NEW MEASUREMENTS

2.1. Experimentation

2.1.1. Test Solutions

ACS reagent grade water was procured from Sigma-Aldrich and directly used for testing. Aqueous sodium chloride solutions were prepared from an original solution of 5M (246.38 g/kg) "Bioultra" aqueous sodium chloride solution purchased from Sigma Aldrich. The original solution was diluted with ACS water to obtain test solutions of salinities $S =$ (39.99, 80.20 and 120.01) g/kg. ASTM seawater solutions were prepared from an original solution of ASTM D1141 substitute ocean water without heavy metals purchased from the Ricca Chemical Company. The original solution of ASTM seawater had a Chlorinity of 19.38 g/kg, which translated to a reference salinity of $S = 35.18$ g/kg with an error of 0.02 g/kg. ASTM seawater test solutions with salinities $S =$ (40.49, 79.39 and 121.54) g/kg were prepared by evaporating and concentrating the ASTM D1141 solution under reduced pressure at $t = 55$ °C using a Buchi R-210 Rotovapor rotary evaporator. Concentration was done in this manner to inhibit the precipitation of sparingly soluble salts. ASTM seawater

of salinity $S = 20.01$ g/kg was prepared by diluting the original solution with ACS water. ASCS seawater ($S = 35.16$ g/kg) procured from OSIL was directly used for testing. The error in salinity quoted by OSIL for ASCS seawater was 0.07 g/kg.

2.1.2. Apparatus

Surface tension was measured to within a resolution of 0.001 mN/m using a Dataphysics DCAT 11 tensiometer employing the Wilhelmy plate method. To ensure a zero contact angle between the Wilhelmy plate and the test solution sample, a Wilhelmy plate made of platinum was selected. A borosilicate glass test beaker was used to contain the test solution sample. The dimensions of the beaker were sufficiently large (diameter 70 mm) when compared with the plate dimensions (length 19.9 mm, width 10 mm and thickness 0.2 mm) to avoid wall effects. To reduce solvent loss through evaporation of the test solution sample and to reduce risks of contamination from the environment, an aluminum lid was used to cover the test beaker. To allow for the easy insertion and movement of the Wilhelmy plate during measurement while still limiting exposure of the sample to the environment, special doors were designed for the lid. To further suppress solvent loss due to condensation on the lid and to minimize natural convection in the test solution sample, the lid was heated using a strip heater controlled by a Proportional-Integral-Derivative (PID) controller to maintain a temperature close to that of the test solution sample. A thermocouple attached to the lid served as an input to the PID controller.

The temperature of the test solution sample was measured using a Fluke 5611T Teflon coated thermistor probe and a Fluke 1524 reference thermometer. The probe and the thermometer were calibrated by the manufacturer to standards traceable to the National Institute of Standards and Technology (NIST) and had a measurement accuracy of 0.01 °C. The small size of the thermistor (diameter 3 mm and sensor length 13 mm) reduced errors arising from self-heating and also allowed for accurate temperature measurements to be made at low immersion depths. Furthermore, the impervious Teflon coating on the probe allowed for easy cleaning and reduced the risk of cross contamination between experiments. Measuring the surface temperature accurately in any experiment is difficult due to challenges in establishing a perfect equilibrium where transport and associated gradients are zero and also due to limitations inherent in immersed temperature probes. Conventionally, experi-

mental studies have immersed probes in test samples while reducing thermal gradients as much as possible, and then equated the measured temperature to be the surface temperature, taking the probe accuracy to be the uncertainty in temperature measurement. In this work, we went a step further and measured the bulk solution temperature corresponding to a surface tension measurement, which unlike surface temperature can be defined more accurately. We stirred the test solution sample with a magnetic stir bar immediately after a surface tension measurement and then measured the temperature. The uncertainty of the bulk solution temperature was 0.03 K. Surface tension was then later correlated to the bulk solution temperature. However, for reference purposes, we also estimated the temperature gradient in the sample by measuring the unstirred temperature corresponding to a surface tension measurement. The difference between stirred and unstirred temperature, at 95% confidence, was 0.07 K for $t < 50$°C and 0.12 K for $t \geq 50$°C.

The salinity of the test solutions and their samples were obtained indirectly by measuring the weight of the solutions. Test solutions were prepared by diluting or concentrating original solutions of known salinities with the initial and final weights being measured using a Mettler Toledo PG2002-S mass balance that had a resolution of 0.01 g and an accuracy of 0.1 g. Evaporation during the experiments caused salinity of the test solution samples to vary during the course of testing. This was characterized by measuring the weights of the test solution samples before and after testing using a Ohaus Scout II SC2040 mass balance that had a resolution and accuracy of 0.01 g. The accuracy of the mass balances was ascertained with the help of reference weights from TA Instruments. The uncertainty in salinity arising from the accuracy of the mass balances was 0.01 g/kg.

2.1.3. Procedure

Glassware was cleaned by rinsing three times with Milli-Q deionized water. The test beaker was rinsed additionally with ACS reagent grade water. Rinsed glassware was dried in an oven before use. During the testing of seawater at elevated temperatures ($t > 50$ °C), precipitation of sparingly soluble salts and scale formation on the test beaker was observed. While precipitation itself did not affect the repeatability of surface tension measurements, accumulation of fine scale on the test beaker over prolonged usage was observed to affect the repeatability[26]. To avoid this problem, new test beakers were used for experiments carried

out on seawater.

Surface tension was measured in test temperature intervals of 10 °C from 0 to 90 °C for each test solution with 3 to 4 test temperatures covered in a single experimental run. Approximately 1 hour was required to achieve steady state at each test temperature. After reaching steady state, 5 to 7 measurements of surface tension and bulk temperature were conducted over another hour to reduce the random error in measurement. Prior to each measurement, the platinum Wilhelmy plate was rinsed in deionized water and cleaned by heating over a flame until the plate was red hot. Surface tension measurements typically stabilized to a near constant value within 1 to 2 measurements. Comparison of measurements of pure water surface tension with the IAPWS correlation for the surface tension of pure water[15] confirmed that stabilized values, typically the last 5 measurements, fit within the accepted uncertainties of the correlation while the initial unstabilized measurements did not. To exclude measurements far from the stabilized value and to include measurements near it, a modified Chauvenet's criterion[27] was applied on the dataset with the last 5 stabilized measurements as a reference sample. Measurements in the dataset which deviated from the mean surface tension of the reference sample by greater than 1.65 times the standard deviation were rejected while measurements that fit within the criteria were included to yield a final dataset of 3 to 6 measurements.

The mass of the test solution sample was measured before and after an experimental run rather than at each test temperature. Thus, the initial and final salinities of an experimental run are known. The salinity corresponding to each surface tension measurement was then calculated by distributing the total mass of solvent lost to evaporation across all surface tension measurements using a weighted average of the vapor pressure difference between the test solution sample and the environment. The model used for this is described in more detail in Appendix A. The accuracy of the model was verified by measuring the intermediate sample weights during some experiments. The standard deviation between calculated and measured salinities was 0.06 g/kg while the maximum deviation was 0.09 g/kg. The maximum deviation of 0.09 g/kg was taken as a conservative estimate of the uncertainty in salinity contributed by the model.

The uncertainty analysis and the experimental procedures have been described in greater detail in the Master's thesis work of the first author[26].

Uncertainty analysis was carried out on measurements as per guidelines recommended

by the Bureau of International Weights and Measurements (BIPM)[28] as well as textbooks written by Patience[29] and Beckwith *et al.*[30] Systematic errors arising from measurement accuracy and random errors in sampling contributed to the combined standard uncertainty (u_c) in temperature and salinity. For salinity, uncertainties arising from preparation, evaporation and from the model in Appendix A were considered as well. Coverage factors (k) used to calculate the expanded uncertainty (U), were evaluated using the inverse of the Student's t-distribution for a 95% confidence interval:

$$k = t_{\text{inv,distrib.}}(0.05, n-1)$$

where n is the number of measurements used for averaging. Typically, the number of measurements was 5 leading to a k value of 2.777. A 95% confidence interval resulted in an average expanded uncertainty in temperature of 0.11 °C and a maximum expanded uncertainty of 0.54 °C. The maximum uncertainty occurred during the testing of aqueous sodium chloride at $t = 87.92$ °C and $S = 123.41$ g/kg. An average combined standard uncertainty in salinity of 0.17 g/kg and a maximum combined standard uncertainty in salinity of 0.82 g/kg was obtained using this approach. The maximum uncertainty in salinity occurred during the testing of ASTM seawater at $t = 87.40$ °C and $S = 130.96$ g/kg. The uncertainty in salinity here included uncertainties in the original solution salinity, preparation procedure, measurement procedure and model used for interpolating salinity.

For surface tension, Type A and Type B uncertainties were separately considered as the coverage factors for evaluating each were different. Random errors in sampling contributed to the combined standard Type A uncertainty and an expanded Type A uncertainty was calculated using the coverage factor described previously. The expanded Type B uncertainty in an average surface tension measurement was calculated by measuring the surface tension of pure water in the temperature range $1 \leq t \leq 92$ °C and comparing the averaged measurements with values calculated from the IAPWS correlation. A 95% confidence interval, and $n = 9$, resulted in an expanded Type B uncertainty of 0.18 mN/m. The root sum of squares of the expanded Type A and Type B uncertainties yielded the final expanded uncertainty in a surface tension measurement.

The uncertainty analysis and the experimental procedures have been described in greater detail in the Master's thesis work of the first author[26].

2.2. Validation

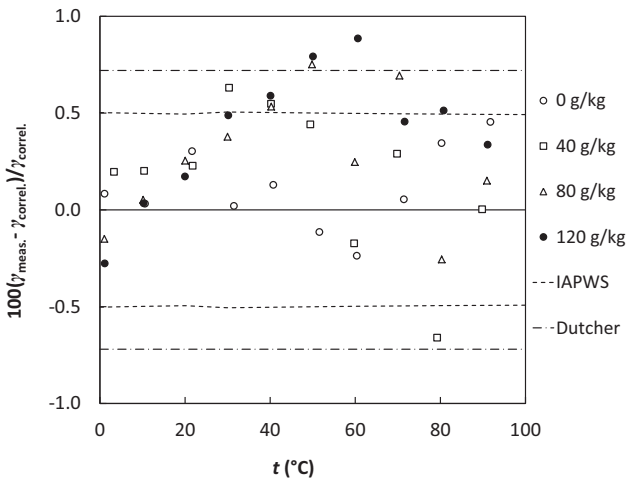


FIG. 1. Percent deviation of surface tension measurements of ACS water and aqueous sodium chloride from the IAPWS correlation[15] and Dutcher's correlation[31], respectively, along with the uncertainty in the IAPWS correlation and average absolute percentage deviation in Dutcher's correlation.

To validate the accuracy of the experimental procedure, surface tension experiments were conducted on ACS water and aqueous sodium chloride solutions at atmospheric pressure for salinities $S = (0, 39.99, 80.19, 120.01)$ g/kg across a temperature range of $t = 0$ - 90 °C, and the results were compared with correlations from literature. For ACS water, the results were compared with the IAPWS correlation for the surface tension of water[15] and for aqueous sodium chloride the results were compared with the correlation developed by Dutcher *et al.*[31]. The comparison was carried out by calculating the percentage deviation of measurements from the correlations as follows:

$$PD = \frac{(\gamma_{\text{meas.}} - \gamma_{\text{correl.}})\,100}{\gamma_{\text{correl.}}} \tag{1}$$

The percentage deviation for the measurements along with the uncertainty in the IAPWS correlation for pure water and the reported average absolute percentage deviation in Dutcher's correlation is depicted in Fig. 1 while the measurements themselves are listed in Appendix B. All surface tension measurements carried out on ACS water fit within the 0.5% uncertainty of the IAPWS correlation with the maximum deviation being 0.45% at

t = 91.75 °C. All sodium chloride measurements with the exception of three high salinity datapoints fit within the 0.72% average absolute percentage deviation of Dutcher's correlation. The maximum percentage deviation for sodium chloride measurements in this work was 0.89% at t = 60.60 °C and S = 123.41 g/kg. To verify that this was within the maximum percentage deviation from Dutcher's correlation, high salinity aqueous sodium chloride measurements from Abramzon *et al.*[32] that Dutcher had used to make the correlation were compared with values calculated from the correlation. The comparison showed that the correlation deviated from Abramzon *et al.*'s data by 1.71% at S = 100 g/kg and t = 60 °C. Thus, a 0.89% deviation observed in this experiment still falls within the deviations of Dutcher's correlation. Thus, it can be concluded that the experimental procedure was both valid and accurate.

2.3. Surface tension of ASTM seawater

TABLE 1: Measurements for ASTM seawater

Sl. No.	S (g/kg)	$u_c(S)$ (g/kg)	t °C	$U(t)$ °C	γ (mN/m)	$U(\gamma)$ (mN/m)	n	k
1	20.20	0.09	0.78	0.28	76.098	0.200	5	2.776
2	20.18	0.10	9.92	0.19	74.802	0.190	5	2.776
3	20.01	0.09	19.90	0.09	73.389	0.207	5	2.776
4	20.04	0.09	30.00	0.09	71.805	0.200	5	2.776
5	20.11	0.09	40.17	0.20	70.195	0.253	5	2.776
6	20.23	0.10	50.45	0.16	68.555	0.233	4	3.182
7	20.42	0.10	60.45	0.05	66.807	0.197	5	2.776
8	20.27	0.10	70.89	0.15	64.932	0.196	5	2.776
9	20.57	0.11	80.43	0.25	63.121	0.248	5	2.776
10	21.21	0.13	90.51	0.08	61.344	0.252	5	2.776
11	35.47	0.09	1.23	0.13	76.389	0.216	5	2.776
12	35.47	0.09	10.05	0.04	75.033	0.250	5	2.776
13	35.28	0.11	20.92	0.03	73.477	0.228	5	2.776

Continued on next page

TABLE 1 – *Continued from previous page*

Sl. No.	S (g/kg)	$u_c(S)$ (g/kg)	t °C	$U(t)$ °C	γ (mN/m)	$U(\gamma)$ (mN/m)	n	k
14	35.20	0.09	30.03	0.03	72.257	0.203	5	2.776
15	35.38	0.10	39.85	0.03	70.562	0.271	5	2.776
16	35.54	0.21	49.73	0.04	69.091	0.240	5	2.776
17	35.85	0.11	59.46	0.08	67.592	0.212	5	2.776
18	35.48	0.10	72.36	0.22	65.170	0.195	5	2.776
19	36.36	0.15	79.50	0.03	63.717	0.215	5	2.776
20	37.64	0.27	90.02	0.19	61.889	0.266	5	2.776
21	40.79	0.09	2.88	0.12	76.425	0.203	5	2.776
22	40.78	0.09	10.37	0.03	75.361	0.245	5	2.776
23	40.53	0.10	19.99	0.08	73.871	0.187	5	2.776
24	40.52	0.09	29.98	0.06	72.516	0.203	5	2.776
25	40.61	0.09	40.37	0.08	70.952	0.216	6	2.571
26	40.76	0.10	50.58	0.09	69.351	0.198	5	2.776
27	40.82	0.11	60.48	0.06	67.383	0.239	5	2.776
28	41.16	0.12	70.29	0.22	65.831	0.207	5	2.776
29	41.64	0.17	79.96	0.07	64.218	0.207	5	2.776
30	42.80	0.26	92.07	0.22	62.106	0.302	5	2.776
31	79.90	0.09	2.28	0.11	77.580	0.233	4	3.182
32	79.82	0.09	10.07	0.19	76.496	0.188	5	2.776
33	79.85	0.09	19.58	0.11	75.229	0.192	5	2.776
34	79.86	0.11	29.98	0.03	73.715	0.208	4	3.182
35	79.49	0.10	40.16	0.25	71.999	0.237	4	3.182
36	79.73	0.11	50.85	0.29	70.193	0.209	4	3.182
37	79.94	0.24	60.80	0.03	68.536	0.352	3	4.303
38	80.64	0.23	70.65	0.06	66.978	0.203	4	3.182
39	81.74	0.26	80.09	0.16	65.191	0.202	5	2.776

Continued on next page

TABLE 1 – *Continued from previous page*

Sl. No.	S (g/kg)	$u_c(S)$ (g/kg)	t °C	$U(t)$ °C	γ (mN/m)	$U(\gamma)$ (mN/m)	n	k
40	83.71	0.64	90.53	0.04	63.507	0.263	4	3.182
41	121.54	0.11	2.29	0.05	78.754	0.184	5	2.776
42	121.56	0.11	9.82	0.06	77.901	0.192	6	2.571
43	122.17	0.11	19.92	0.04	76.669	0.189	5	2.776
44	121.65	0.11	30.01	0.03	75.189	0.194	5	2.776
45	121.82	0.11	40.22	0.13	73.767	0.207	6	2.571
46	122.20	0.14	51.48	0.09	72.241	0.193	5	2.776
47	122.86	0.15	60.86	0.04	70.493	0.194	5	2.776
48	123.89	0.18	71.21	0.05	68.896	0.224	7	2.447
49	126.49	0.25	80.68	0.06	67.130	0.207	5	2.776
50	130.96	0.82	87.40	0.48	66.109	0.375	4	3.182

Surface tension of ASTM seawater of initial reference salinities S = (20.01, 35.18, 40.49, 79.39, 121.54) g/kg was measured at atmospheric pressure across a temperature range of 1 to 92 °C in intervals of 10 °C. A total of 245 measurements were averaged and uncertainty analysis was performed to give a final set of 50 average measurements of salinity (S), temperature (t), and surface tension (γ). Table 1 lists these with the corresponding uncertainties — combined standard uncertainty for salinity ($u_c(S)$) and expanded uncertainty for bulk temperature ($U(t)$) and surface tension ($U(\gamma)$) — along with the number of measurements at each temperature and salinity (n) and the coverage factor (k) used to calculate the expanded uncertainty.

The uncertainty in the average surface tension measurements is depicted in Fig. 2. The maximum uncertainty was 0.375 mN/m at t = 87.40 °C and S = 130.96 g/kg while the minimum uncertainty was 0.184 mN/m at t = 2.29 °C and S = 121.54 g/kg. The average uncertainty for all measurements was 0.223 mN/m.

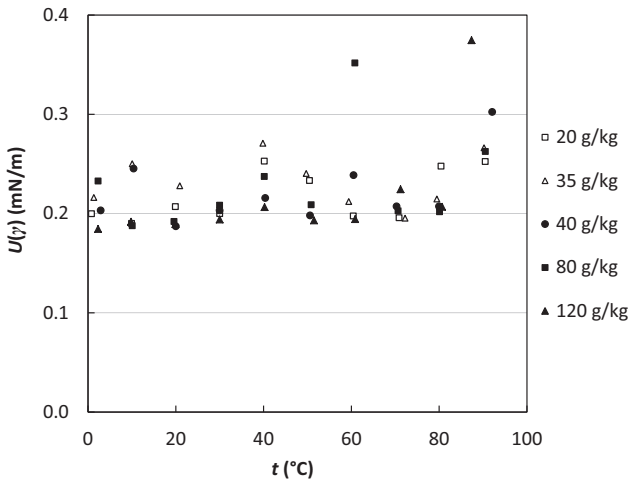


FIG. 2. Expanded uncertainty in surface tension measurements for ASTM seawater

TABLE 2. Measurements for ASCS seawater

Sl. No.	S (g/kg)	$u_c(S)$ (g/kg)	t °C	$U(t)$ °C	γ (mN/m)	$U(\gamma)$ (mN/m)	n	k
1	35.20	0.11	1.11	0.05	76.307	0.196	6	2.571
2	35.20	0.11	9.67	0.03	74.977	0.190	4	3.182
3	35.18	0.11	19.55	0.03	73.695	0.451	5	2.776
4	35.17	0.11	29.80	0.05	72.367	0.241	3	4.303
5	35.22	0.11	40.17	0.11	70.801	0.187	5	2.776
6	35.27	0.12	50.83	0.34	69.075	0.200	5	2.776
7	37.70	0.14	60.81	0.27	67.147	0.217	4	3.182
8	38.07	0.15	70.66	0.22	65.348	0.217	5	2.776
9	38.72	0.18	80.40	0.09	63.945	0.219	5	2.776
10	36.00	0.39	90.53	0.19	61.719	0.309	6	2.571

2.4. Surface tension of ASCS seawater

Surface tension of ASCS seawater of initial reference salinity $S = 35.16$ g/kg was measured at atmospheric pressure across a temperature range of 1 to 91 °C in intervals of 10 °C. A total of 48 measurements were averaged and an uncertainty analysis was performed to obtain

TABLE 3. Measurements of surface tension of seawater at atmospheric pressure

1st author	Year	Technique	Seawater	t (°C)	S (g/kg)	No. points	Uncertainty (%)
			Primary data				
Nayar[a]	2014	Wilhelmy plate	ASTM	1 - 92	0 - 131	50	0.23 - 0.57
			Secondary data				
Krummel[5]	1900	Jaeger's method[14]	North Sea	13 - 14	8 - 35	5	1.35
Chen[6]	1994	MBP[b]	North Pacific	15 - 35	5 - 35	60	>0.2
Schmidt[7]	2011	Wilhelmy plate	Baltic, Atlantic	5 - 30	0 - 35	18	na[c]
Nayar[a]	2014	Wilhelmy plate	ASCS	1 - 91	35 - 39	10	0.25 - 0.61

[a] Present work
[b] Maximum bubble pressure
[c] na: not available

a final set of 10 average measurements of salinity, temperature and surface tension. These values along with their uncertainties are listed in Table 2. The maximum uncertainty was 0.451 mN/m at a $t = 19.55$ °C and $S = 35.18$ g/kg while the minimum uncertainty was 0.187 mN/m at $t = 40.17$ °C and $S = 35.22$ g/kg. The average uncertainty of all measurements was 0.243 mN/m.

3. CORRELATION

3.1. Primary data

A summary of seawater surface tension measurements from previous studies as well as the present work is given in Table 3. For the primary dataset, surface tension measurements on ASTM seawater carried out in this work were used. These represent the most accurate seawater surface tension measurements that extend to high temperature and salinity that is currently available.

Other datasets were categorized as secondary, as they used natural seawater samples that may have contained organic surface active material, or did not reliably quantify the Type

A and B uncertainty (by repeating measurements at each temperature and salinity or by measuring the surface tension of a reference fluid and comparing results with a reference dataset or by inference from the information reported by the experimenter), or showed higher uncertainty in the temperature and salinity range considered. Measurements from Krummel and Chen *et al.* were not considered as primary because organic surfactants may have been present in their natural seawater samples. Additionally, Krummel's measurements were not included because of a high Type B uncertainty arising from differences between Krummel's value for the surface tension of pure water and the current IAPWS correlation for the surface tension of pure water. Furthermore, Krummel's measurements were restricted to only one temperature and for half the samples, surface tension was measured only once. In the dataset of Chen *et al.*, the Type A and B uncertainties were not adequately quantified and could not be accurately estimated; the Type A uncertainty could not be evaluated as surface tension data was reported only once at each temperature and salinity while the Type B uncertainty seemed to be high as the final reported correlation deviated by up to 0.66% from the IAPWS pure water correlation at zero salinity. While Schmidt *et al.* measured surface tension of seawater rigorously by removing the surfactants in seawater, raw data was reported in a plot and was not readily available for consideration as accurate primary data. Smoothed data was available from a correlation for the surface tension of seawater that was reported by Schmidt *et al.* — however, the deviation of seawater surface tension measurements from the correlation was not reported. Furthermore, a complete uncertainty analysis of seawater surface tension measurements was also not reported. For these reasons, the dataset of Schmidt *et al.* was considered secondary. Surface tension measurements of ASCS seawater from the present study were considered as secondary data because the presence of surface active materials in the sample was not irrefutable.

Primary data was fit to obtain the following best fit correlation:

$$\gamma_{\mathrm{sw}} = \gamma_{\mathrm{w}} \left[1 + 3.766 \times 10^{-4}\ S + 2.347 \times 10^{-6}\ S\ t\right] \tag{2}$$

where, γ_{sw} is surface tension of seawater in mN/m, S is reference salinity in g/kg, and t is temperature in Celsius in the current ITS-90 temperature scale and γ_{w} is the surface tension

of pure water in mN/m as calculated from the IAPWS correlation given by:

$$\gamma_{\mathrm{w}} = 235.8 \left(1 - \frac{t + 273.15}{647.096}\right)^{1.256} \times \left[1 - 0.625 \left(1 - \frac{t + 273.15}{647.096}\right)\right] \tag{3}$$

The form of the fit was similar to that used by Chen *et al.* and is a simple function generally used to describe the variation of surface tension of aqueous electrolytes at low salt concentrations[31].

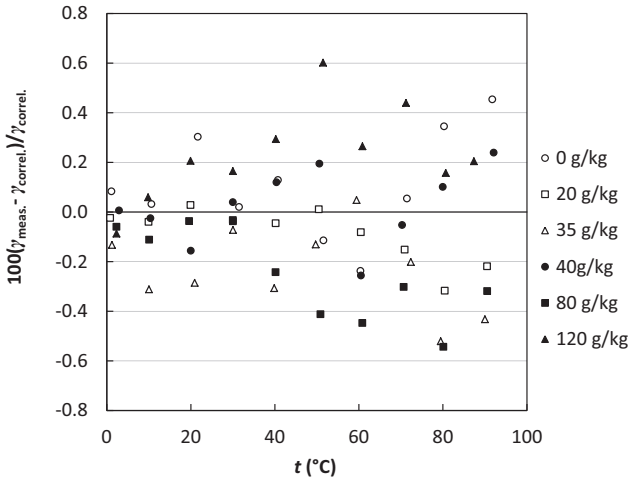


FIG. 3. Deviation of surface tension measurements for ASTM seawater from surface tension calculated by Eq. 2.

The fit had a coefficient of determination (R^2) value of 0.999. The percentage deviation between the primary data and values calculated from Eq. 2 is depicted in Fig. 3. The average absolute percentage deviation of data from the fit was 0.19% while the maximum percentage deviation was +0.60% at t = 51.48 °C and S = 122.20 g/kg. A comparison of some of the primary data with the fit is depicted in Fig. 4.

3.2. Secondary Data

The percentage deviation between secondary data and the values calculated from the correlation given by Eq. 2 is depicted in Fig. 5. Krummel's dataset deviated the most with an average absolute percentage deviation of 1.05%. The high deviation is reflective

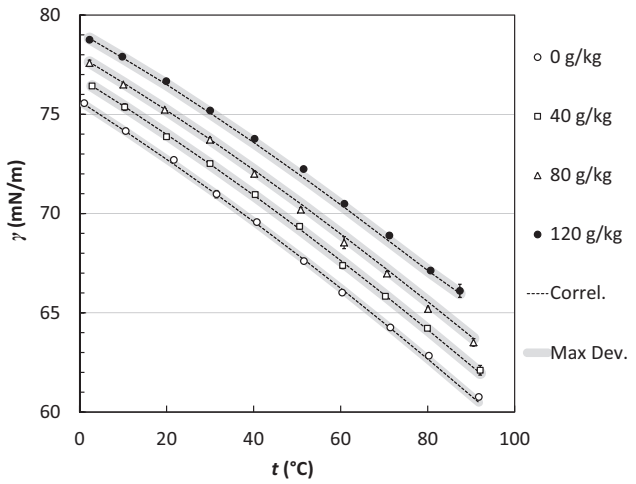


FIG. 4. Select surface tension measurements compared to the correlation given in Eq. 2 along with the maximum deviation of the correlation.

of the 1 mN/m difference between surface tension values of pure water used by Krummel and values calculated from the current IAPWS correlation for pure water. Smoothed data from Schimdt *et al.* deviated the least with a average absolute percentage deviation of 0.06%. This is reasonable as the natural seawater samples of Schmidt *et al.*, like the ASTM seawater samples used for primary data in the present study, did not contain any surface active organic content. Chen's dataset showed an average absolute percentage deviation of 0.20% while the maximum percentage deviation was -0.47% at t = 14.778 °C and S_{P} = 34.486. Measurements carried out on ASCS seawater in the present work showed an average absolute percentage deviation of 0.26% while the maximum percentage deviation was -0.52% at S = 38.07 g/kg and t = 70.66 °C. The average absolute percentage deviations of Chen's dataset and the ASCS dataset were within the 0.6% maximum percentage deviation of the reference correlation. Trace organic content in seawater samples of Chen *et al.* and ASCS seawater did not significantly reduce the reported surface tension. Thus, the values for surface tension of seawater obtained from the reference correlation extends reasonably well to properly treated natural seawater. From the above analysis of secondary data, it can also be concluded that the reference correlation predicts the surface tension of natural seawater in the absence of surfactants.

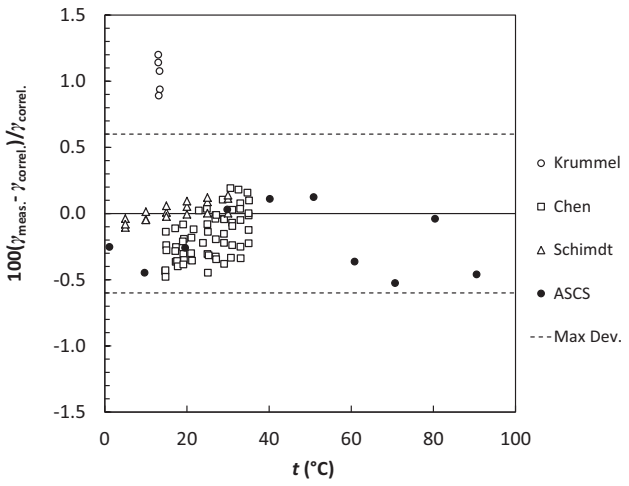


FIG. 5. Deviation of seawater surface tension data of Krummel[5], Chen *et al.*[6], Schmidt *et al.*[7] and 35 g/kg ASCS seawater measurements presented in this work from surface tension calculated using Eq. 2 along with the 0.6% maximum percentage deviation of ASTM seawater measurements from Eq. 2.

4. CONCLUSION

Surface tension of ASTM seawater was measured accurately at atmospheric pressure across a temperature range of $1 \leq t \leq 92$ °C and a salinity range of $0 \leq S \leq 131$ g/kg. The uncertainty in measurements varied between 0.18 - 0.37 mN/m (0.23 - 0.57 %). A reference correlation for the surface tension of seawater as a function of temperature and salinity was developed. The average absolute percentage deviation of measurements from the correlation was 0.19% while the maximum percentage deviation was 0.60%. The reference correlation is valid across a temperature range of $1 \leq t \leq 92$ °C and a salinity range of $0 \leq S \leq 131$ g/kg, and can be safely extrapolated to the temperature range $0 \leq t \leq 100$ °C. Extrapolating the correlation beyond a salinity of 131 g/kg or a temperature of 100 °C is not recommended as increased precipitation of sparingly soluble salts under these conditions may cause surface tension of seawater to vary differently.

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Appendix A: Salinity Model

Salinity was not measured at each test temperature but before and after an interval of 3 to 4 test temperatures. The initial salinity (S_{initial}) is known from test solution preparation and the final salinity (S_{final}) of the test solution sample is obtained by measuring the total mass of solvent lost ($m_{\text{solv,loss,total}}$). The loss in solvent mass resulted from evaporative losses that occurred despite the presence of the lid. The salinity (S_i) corresponding to each surface tension measurement is calculated as follows:

1. The rate of loss of solvent due to evaporation at any instant is approximately proportional to the difference in vapor pressure of water vapor above the test solution surface ($P_{\text{vap,surf}}$) and vapor pressure of water vapor in the environment ($P_{\text{vap,env}}$).

$$\frac{\mathrm{d}m_{\text{solv,loss}}}{\mathrm{d}t} = B(P_{\text{vap,surf}} - P_{\text{vap,env}}) \tag{A1}$$

   The constant of proportionality (B) is a function of the geometry of the lid and test procedures, and is approximated as a constant within any one set of measurements. $P_{\text{vap,surf}}$ was approximated by the saturation vapor pressure for pure water at the corresponding solution bulk temperature. $P_{\text{vap,env}}$ was calculated from psychrometry from the relative humidity (RH) and temperature in the environment which due to air-conditioning is approximately held constant at 24 °C and 25% RH. This was measured using a digital hygrometer/thermometer with a NIST traceable calibration, manufactured by the Control Company.

2. The total mass of solvent lost, time duration (Δt_i) between measurements and the vapor pressure difference between the sample and the environment ($\Delta P_{\mathrm{vap},i}$) during each measurement is known and Eq. A1 was discretely integrated across the complete set of surface tension measurements (N_{total}) to obtain a value for 'B' as follows:

$$\Delta P_{\mathrm{vap},i} = P_{\mathrm{vap,surf},i} - P_{\mathrm{vap,env},i} \tag{A2}$$

$$B = \frac{m_{\mathrm{solv,loss,total}}}{\sum_{i=1}^{N_{\mathrm{total}}} \Delta P_{\mathrm{vap},i}\ \Delta t_i} \tag{A3}$$

The mass of solvent lost from the beginning until the end of each surface tension measurement ($m_{\mathrm{solv,loss},i}$) and the salinity corresponding to each surface tension measurement was then obtained as follows:

$$m_{\mathrm{solv,loss},i} = B \sum_{k=1}^{i} \Delta P_{\mathrm{vap},k} \Delta t_k \tag{A4}$$

$$S_i = S_{\mathrm{initial}} \frac{m_{\mathrm{soln,initial}}}{m_{\mathrm{soln,initial}} - m_{\mathrm{solv,loss},i}} \tag{A5}$$

Appendix B: Surface tension measurements of ACS water and aqueous sodium chloride

The average measurements of salinity (S), temperature (t), and surface tension (γ), the uncertainty in measurements, the number of points used for averaging (n), and the coverage factor (k) used for calculating uncertainty for ACS water and aqueous sodium chloride are listed in Tables 4 and 5 respectively.

TABLE 5: Measurements for aqueous sodium chloride

Sl. No.	S (g/kg)	$u_{\mathrm{c}}(S)$ (g/kg)	t °C	$U(t)$ °C	γ (mN/m)	$U(\gamma)$ (mN/m)	n	k
1	40.05	0.09	3.29	0.05	76.526	0.197	5	2.776
2	40.04	0.09	10.37	0.08	75.498	0.185	5	2.776

Continued on next page

TABLE 4. Measurements for ACS water

Sl. No.	S (g/kg)	$u_c(S)$ (g/kg)	t °C	$U(t)$ °C	γ (mN/m)	$U(\gamma)$ (mN/m)	n	k
1	0.00	-	1.07	0.03	75.561	0.199	5	2.776
2	0.00	-	10.59	0.03	74.159	0.218	5	2.776
3	0.00	-	21.65	0.24	72.706	0.188	5	2.776
4	0.00	-	31.47	0.04	70.977	0.256	5	2.776
5	0.00	-	40.73	0.04	69.568	0.194	5	2.776
6	0.00	-	51.55	0.06	67.605	0.205	6	2.571
7	0.00	-	60.35	0.04	66.020	0.190	6	2.571
8	0.00	-	71.42	0.03	64.262	0.191	4	3.182
9	0.00	-	80.27	0.12	62.839	0.196	5	2.776
10	0.00	-	91.75	0.30	60.761	0.198	5	2.776

TABLE 5 – *Continued from previous page*

Sl. No.	S (g/kg)	$u_c(S)$ (g/kg)	t °C	$U(t)$ °C	γ (mN/m)	$U(\gamma)$ (mN/m)	n	k
3	39.99	0.09	21.79	0.03	73.770	0.182	5	2.776
4	40.42	0.10	30.33	0.03	72.755	0.194	5	2.776
5	40.02	0.09	40.21	0.04	71.080	0.213	5	2.776
6	40.36	0.10	49.44	0.05	69.472	0.184	5	2.776
7	40.87	0.17	59.73	0.03	67.300	0.237	6	2.571
8	41.45	0.19	69.82	0.08	65.840	0.225	5	2.776
9	43.68	0.33	79.22	0.07	63.584	0.375	7	2.447
10	41.37	0.35	89.80	0.16	61.972	0.526	5	2.776
11	80.17	0.09	1.05	0.04	77.872	0.191	5	2.776
12	80.28	0.09	10.17	0.03	76.695	0.181	5	2.776
13	80.67	0.11	20.04	0.03	75.358	0.182	6	2.571
14	81.38	0.19	30.00	0.03	73.901	0.199	6	2.571

Continued on next page

TABLE 5 – *Continued from previous page*

Sl. No.	S (g/kg)	$u_c(S)$ (g/kg)	t °C	$U(t)$ °C	γ (mN/m)	$U(\gamma)$ (mN/m)	n	k
15	80.43	0.10	40.27	0.05	72.306	0.182	6	2.571
16	80.72	0.10	49.84	0.06	70.854	0.221	5	2.776
17	80.87	0.23	59.90	0.05	68.762	0.274	5	2.776
18	81.54	0.16	70.40	0.07	67.208	0.197	6	2.571
19	82.44	0.37	80.32	0.08	64.793	0.415	5	2.776
20	84.92	0.51	90.95	0.16	63.138	0.401	5	2.776
21	120.00	0.09	1.12	0.08	79.140	0.185	6	2.571
22	120.03	0.09	10.27	0.05	78.030	0.183	6	2.571
23	120.04	0.10	19.99	0.04	76.644	0.189	5	2.776
24	120.21	0.10	30.15	0.30	75.270	0.187	6	2.571
25	120.52	0.10	40.09	0.04	73.717	0.198	6	2.571
26	120.92	0.13	50.05	0.05	72.184	0.209	5	2.776
27	123.41	0.54	60.60	0.54	70.482	0.234	5	2.776
28	121.22	0.19	71.60	0.50	68.127	0.206	5	2.776
29	122.63	0.31	80.76	0.17	66.521	0.205	5	2.776
30	124.61	0.50	91.11	0.12	64.515	0.214	6	2.571

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