Effect of Temperature on the Surface Tension of Soluble and Insoluble Surfactants of Hydrodynamical Importance

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The effect of temperature on the surface tension of soluble and insoluble surfactants was investigated at an air−water interface. Equilibrium surface tension measurements were performed using the Wilhelmy plate technique in which both temperature and concentration were varied systematically. Insoluble surfactants (oleyl alcohol and hemicyanine) and soluble surfactants (Triton X-100 and sodium dodecyl sulfate (SDS)) were used since they are commonly used in hydrodynamic experiments in which the effects of surfactants on free surface dynamics are studied. The principal result of this investigation is that the surface tension of the above-mentioned surfactants decreases linearly with temperature, independent of concentration, with the exception of oleyl alcohol whose surface tension becomes relatively independent of temperature above 23 °C. The adequacy of standard models for surfactant behavior in describing these data is considered.

Introduction

Surfactants can have a significant impact on a wide variety of interfacial hydrodynamical transport processes occurring at air−water interfaces. Many of these effects can be explained by virtue of the elasticity imparted to the interfacial region by the surfactant. Examples of important processes affected or caused by surfactants include (A) the damping of capillary waves,[1,2] (B) the modification of vortex-free surface interactions,[3−6] (C) the damping of subsurface turbulence,[7−10] (D) the modification of gas transport,[11−19] and (E) the alteration of wave breaking dynamics.[20] Sarpkaya[21] has given a comprehensive review of many of the studies cited above in addition to discussing the relevant hydrodynamical background.

The effects of surfactants on heat transport at the air−water interface have also attracted considerable attention.[22−24] More recent efforts have exploited new measurement technologies such as high-resolution infrared (IR) sensors to reveal the interfacial dynamics in great detail. In particular, IR focal plane array based sensors, which typically have thermal resolutions of 0.02 K[9,25,26] and also high spatial and temporal resolution, have been used to study interfacial dynamics with special emphasis on surfactant dynamics. Most recently, the interaction of wind shear with a contaminated air−water interface was examined using IR imaging.[27,28] These experiments revealed that wind shear compresses the surfactant film against a stationary barrier, generating a so-called wind-driven Reynolds-ridge. The compressed surfactant results in an interface that is (1 to 2) K cooler than the surrounding clean surface and since the Reynolds-ridge itself is only millimeters in width; the temperature gradients at these fronts can be very large.

It is therefore possible that temperature-induced surface tension changes as well as concentration-induced changes can be important in these frontal regions. These observations motivate, in part, the experiments to be described below where we have studied the effects of concentration and, more importantly, temperature on the surface tension of two insoluble (oleyl alcohol and hemicyanine) and soluble (Triton X-100 and sodium dodecyl sulfate (SDS)) surfactants. These surfactants were chosen primarily because they have been traditionally the most frequently used in many of the hydrodynamical investigations described above. We have also chosen temperature and concentration ranges commonly used in many laboratory investigations involving the hydrodynamical effects of surfactants. It is hoped that these data will be useful in determining the role played by temperature in determining the properties of these commonly used surfactants.

Experimental Section

Apparatus. The experiments were conducted in a computer controlled Langmuir trough facility (see Figure 1). The trough is 57 cm × 17 cm × 0.9 cm and constructed from 1.5 mm thick solid PTFE (Teflon) and mounted on a temperature-regulated base plate. The total volume was approximately 1 L. The surface tension was measured using a Wilhelmy plate (KSV 5000 Langmuir−Blodgett Instrument). Temperature control was achieved by circulating aqueous glycol from a temperature-controlled bath (Julabo USA, model FE500) through the thermoregulated base plate. The cooler had a fine scale digital setting that ranges from −25 °C to 40 °C and was used to maintain the temperature to within ± 0.1 °C.

Cleaning Process. The cleaning process is of paramount importance when making surface tension measurements. The surfaces that come into contact with the liquid were cleaned thoroughly and carefully with HPLC-grade methanol and then with doubly distilled water to avoid any contamination in the system. This process was repeated several times prior to starting the experiments.

Barriers made out of hydrophilic material (Teflon) were placed on both sides of the arm-locked positions of the

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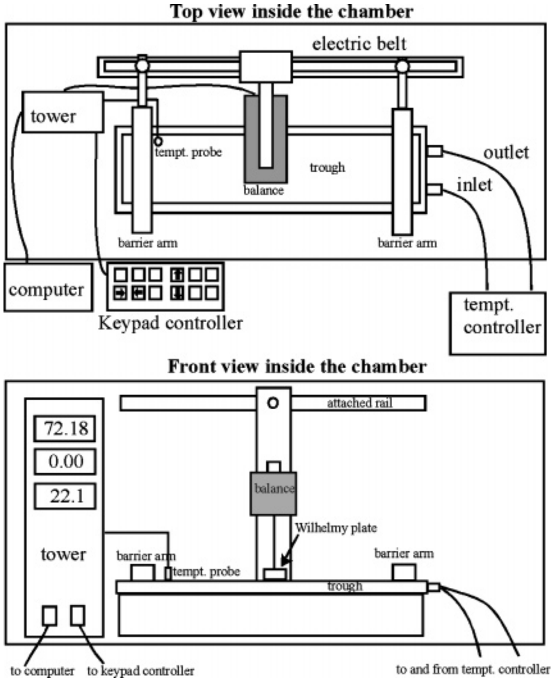

Figure 1. Experimental setup showing top and front views.

trough. The trough was then filled with doubly distilled water until the water surface touched the barriers. The water was permitted to sit for about 30 min in order for any remaining naturally occurring surfactant to diffuse to the surface. To consolidate and remove this contamination from the system, the barriers were moved so as to confine the unwanted material to a small area. A sterile syringe was then used to suction off the top fluid layer.

Surfactants. As mentioned above, the insoluble (oleyl alcohol, hemicyanine) and soluble (Triton X-100, SDS) surfactants used in this study have been used for many experimental studies in the literature. Some of their properties such as surface tension have been determined over a range of concentrations. Oleyl alcohol has been shown to exhibit characteristics similar to natural surfactants found on ocean surfaces.[29] Hemicyanine is a solid fluorescent dye material.[30,31] It gives strong second harmonic emission when probed with the appropriate laser radiation[32,33] and has been used in several air−water free surface experiments because of its insolublity.[20,34] Triton X-100 is one of the popular nonionic detergents used to solubilize membrane proteins and to conduct gas chromatography.[35] It has been used in the study of droplet impact dynamics[36,37] and in the study of breaking waves.[20,34] The anionic surfactant SDS is commonly used as an agent for its wetting, foaming, and dispersing properties.[38−40] In addition, it has the ability to separate proteins and lipids electrophoretically.[41]

Oleyl alcohol (IUPAC: *cis*-9-octadecen-1-ol; CAS Registry No.: 143-28-2; molecular weight (MW) = 268.5 g/mol), Triton X-100 (IUPAC: *tert*-octylphenoxypolyethoxyethanol; CAS Registry No.: 9002-93-1; MW = 250.4 g/mol), and hemicyanine (IUPAC: 4-[4-(dimethylamino)styryl]-1-docosylpyridinium bromide; CAS Registry No.: 103998-45-4; MW = 613.80 g/mol) were all purchased from the Aldrich Chemical Co. SDS (Catalog No. 351-032-060; MW = 288.4 g/mol) was the molecular biology grade product from Quality Biological, Inc. Since both oleyl alcohol and hemicyanine are insoluble in water, their concentrations are based on the spreading area. In contrast, both Triton X-100 and SDS are soluble in water; therefore, their concentrations are based on bulk volume. In the experiments described below, the surfactant concentrations were chosen to conform to the concentrations reported in the literature.

Formation of Monolayers. A stock solution of oleyl alcohol, which was created by mixing it with laboratory grade heptane (CAS Registry No.: 142-82-5; MW = 100.20 g/mol), was withdrawn and deposited onto the free surface with a microliter syringe to form a monolayer. To ensure that the heptane was completely evaporated, each drop was deposited slowly until reaching the desired concentration, ranging from 0.027 mg·m^{-2} to 0.101 mg·m^{-2}.

Hemicyanine was dissolved in doubly distilled water to obtain a stock solution with a concentration of 1.08 g·L^{-1} in concentration. To completely dissolve it, the solution was placed in an ultrasonic bath for a period of 2 days. The final solution has a bright orange color. An appropriate quantity was withdrawn and deposited onto the free surface at the center of the trough via a microsyringe. The hemicyanine experiments were run at different surface concentrations, ranging from 0.059 mg·m^{-2} to 0.235 mg·m^{-2}.

Triton X-100 was mixed with doubly distilled water to obtain a stock solution with a concentration of 21.4 g·L^{-1}. A volume was withdrawn and added to the trough. As this surfactant has a tendency to generate bubbles, which may alter surfactant properties, care was taken to ensure that none were produced. The bulk concentrations in these experiments ranged from 0.52 mg·L^{-1} to 7.83 mg·L^{-1}. The monolayer preparation procedure for SDS was the same as described for Triton X-100. The concentrations ranged from 6.27 mg·L^{-1} to 33.8 mg·L^{-1}.

Surface Tension Measurement. For all cases examined, the Wilhelmy plate was located in the middle of the trough (see Figure 1). The plate was flamed periodically with a commercial propane torch to eliminate any organic substances, and was soaked in HPLC-grade methanol for approximately 10 min prior to all experimental runs. Prior to hanging the plate on the measuring system, it was rinsed with doubly distilled water. The surface area occupied by the surfactant may be changed by using a precision screw driven by an electric drive. In these experiments, however, the surface concentration was changed by adding surfactant material to a fixed surface area. This fixed surface area (0.0984 m^2) was the same for experimental runs. The surface tension of a clean water surface was always measured prior to each surfactant run. It has been reported in the literature that the surface tension of clean water at 22 °C is (73.1 ± 0.013) mN·m^{-1}.[42] In the present study, the average value was (72.8 ± 0.02) mN·m^{-1} at 22 °C. Experimental runs were initiated only when the surface tension matched this value.

The trough temperature was monitored with a thermistor provided with the KSV 5000 system. This sensor was located on the left side of the trough, as shown in Figure 1. The temperature was varied from 15 °C to 35 °C in increments of 2 °C. All data (time, surface tension, and temperature) were recorded via computer. Although we did not repeat any of the experiments, we averaged the surface tension and temperature data over 5-min intervals which resulted in error estimates of ± 0.03 mN·m^{-1} for surface tension and ± 0.01 °C for temperature.

In this study, the two soluble surfactants required careful attention in order to obtain accurate surface tension measurements. Preliminary studies showed that the equilibrium surface tension of Triton X-100 occurred approximately 8 h after the monolayer was formed. The time period in this study was shorter than that reported by Saylor[36] and Saylor and Grizzard,[37] which was about 13

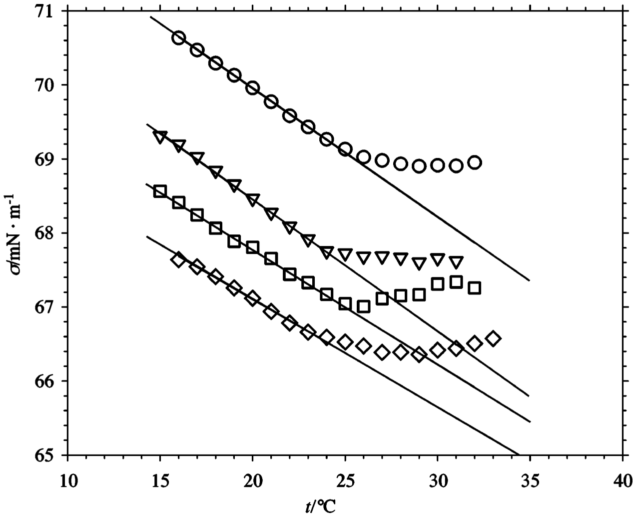

Figure 2. Variation of oleyl alcohol (surface tension standard deviation: ± 0.03 mN·m^{-1}) with temperature at various concentrations: ○, 0.027 mg·m^{-2}; ▽, 0.040 mg·m^{-2}; □, 0.053 mg·m^{-2}; ◇, 0.101 mg·m^{-2}. The solid lines are the best fit lines (eq 1) at each concentration using the fitted parameters given in Table 5.

h. It was speculated that this time difference was related to differences in bulk volume; the volume in this study was approximately 1 L while the volume in Saylor's study was approximately 2.5 L. To ensure that the system reached its asymptotic surface tension, each solution was allowed to equilibrate for 16 h before each run.

Similar to Triton X-100, SDS reached its asymptotic surface tension value after approximately 8 h. Generally, as the concentration of aqueous SDS increases, the time for the surface tension to reach its equilibrium value decreases.[43] The data presented therein indicate that it would take approximately 5 h at a concentration of 115 mg·L^{-1} (4 × 10^{-4} mol·L^{-1}) for the surface tension to reach its asymptotic value. Therefore, all SDS measurements were recorded after at least 10 h.

Results and Discussion

Plots of the surface tension (σ) against temperature (t), given in °C, over a range of surface concentrations for oleyl alcohol, hemicyanine, Triton X-100, and SDS monolayers are shown in Figures 2, 3, 4, and 5, respectively. The raw data used to construct these plots are listed in Tables 1 to 4. As discussed above, we estimate the error in our surface tension measurements to be ± 0.03 mN·m^{-1}. Here γ and c define the surface concentration and the bulk concentration, respectively. In regions where we expect linearity to hold, we have determined the best fit straight line in the least squares sense. The linear fit was of the form:

$$\sigma = A + Bt \qquad (1)$$

where $B = \mathrm{d}\sigma/\mathrm{d}t$ and A, along with the goodness of fit parameters, R^2 (the correlation coefficient), are given in Table 5. It can be seen that R^2 values are very near one in all cases indicating that a linear fit is entirely appropriate and accurate. The best fit lines given by eq 1 are also plotted in Figures 2, 3, 4, and 5.

The surface tension values for oleyl alcohol throughout the concentration range considered here at 22 °C were in agreement with those reported by Saylor.[36] The maximum difference between our results and Saylor's is 4.2 %. Comparison of the present results and the results of Saylor with the data of Vogel and Hirsa[33] at 22.5 °C shows differences primarily at low concentrations (2.0 × 10^{-4} g·m^{-2} to 7.5 × 10^{-4} g·m^{-2}). In this regime, Vogel and Hirsa see very little surface tension change. We suspect that the reason for this discrepancy may be that in Saylor's and our own work, a volumetric technique was used to determine the concentration while Vogel and Hirsa utilized second harmonic generation (SHG), which is inherently an indirect means of determining concentration. This leads us to suspect that SHG may not be very sensitive at these low concentrations. In this regard, it is interesting to note that Saylor has shown that such low concentrations of surfactant can impact the surface tension and that very low concentrations can be detected using an IR imaging technique.[26] Evidence for this is also given in several recent papers.[27,28] The best fit straight line for the oleyl alcohol data shown in Figure 2 were determined from the data below and including t = 23 °C since it is apparent that surface tension is no longer linearly related to temperature beyond approximately this temperature. Instead, the sur-

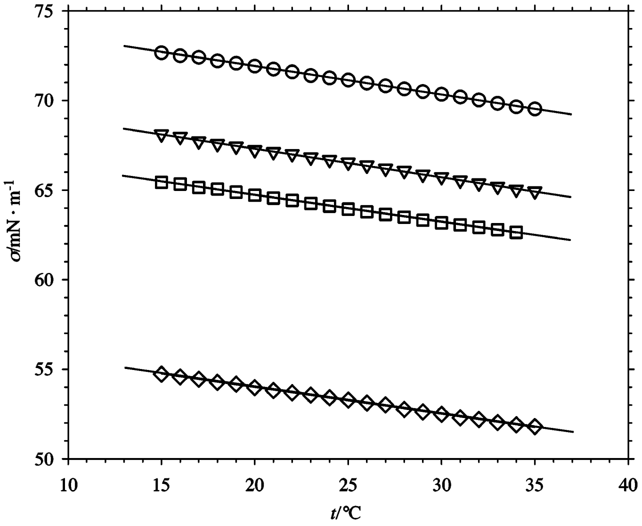

Figure 3. Variation of hemicyanine (surface tension standard deviation: ± 0.03 mN·m^{-1}) with temperature at various concentrations: ○, 0.059 mg·m^{-2}; ▽, 0.105 mg·m^{-2}; □, 0.159 mg·m^{-2}; ◇, 0.235 mg·m^{-2}. The solid lines are the best fit lines (eq 1) at each concentration using the fitted parameters given in Table 5.

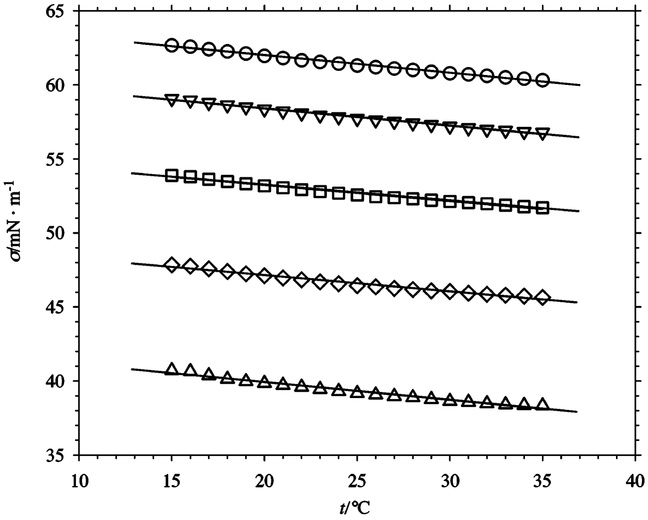

Figure 4. Variation of Triton X-100 (surface tension standard deviation: ± 0.03 mN·m^{-1}) with temperature at various concentrations: ○, 0.52 mg·L^{-1}; ▽, 1.03 mg·L^{-1}; □, 2.24 mg·L^{-1}; ◇, 3.86 mg·L^{-1}; △, 7.83 mg·L^{-1}. The solid lines are the best fit lines (eq 1) at each concentration using the fitted parameters given in Table 5.

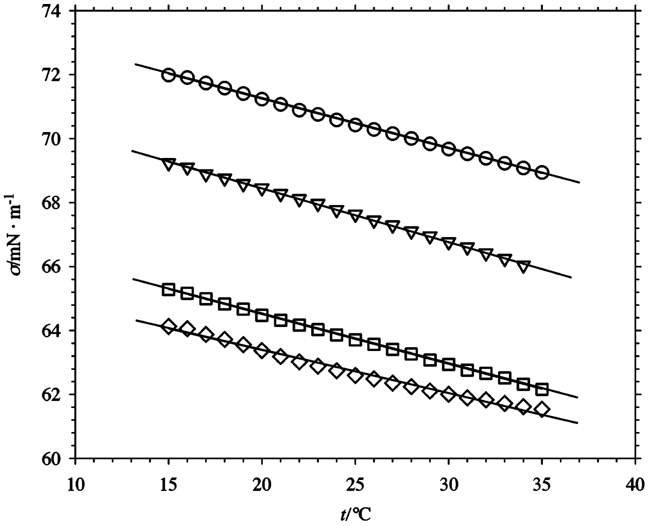

Figure 5. Variation of SDS (surface tension standard deviation: ± 0.03 mN·m^{-1}) with temperature at various concentrations: ○, 6.27 mg·L^{-1}; ▽, 15.7 mg·L^{-1}; □, 27.3 mg·L^{-1}; ◇, 33.8 mg·L^{-1}. The solid lines are the best fit lines (eq 1) at each concentration using the fitted parameters given in Table 5.

Table 1. Surface Tension Values of Oleyl Alcohol at Various Concentrations and Temperatures[a]

	c/(mg·m^{-2})			
	0.0265	0.0398	0.0530	0.101
t/°C	σ/(mN·m^{-1})			
15		69.31	68.56	
16	70.64	69.20	68.41	67.67
17	70.47	69.03	68.24	67.57
18	70.29	68.84	68.06	67.41
19	70.13	68.66	67.89	67.26
20	69.96	68.47	67.81	67.12
21	69.77	68.28	67.65	66.94
22	69.58	68.09	67.44	66.78
23	69.43	67.92	67.33	66.66
24	69.27	67.75	67.17	66.59
25	69.13	67.73	67.04	66.53
26	69.02	67.68	67.01	66.47
27	68.98	67.69	67.11	66.39
28	68.93	67.67	67.15	66.39
29	68.91	67.61	67.17	66.36
30	68.91	67.66	67.31	66.42
31	68.90	67.62	67.34	66.44
32	68.95		67.26	66.51
33				66.57

[a] Surface tension standard deviation: ± 0.03 mN·m^{-1}.

Table 2. Surface Tension Values of Hemicyanine at Various Concentrations and Temperatures[a]

	c/(mg·m^{-2})			
	0.0587	0.105	0.159	0.235
t/°C	σ/(mN·m^{-1})			
15	72.66	68.12	65.44	54.72
16	72.50	67.98	65.33	54.56
17	72.41	67.72	65.14	54.44
18	72.21	67.58	65.05	54.26
19	72.08	67.44	64.88	54.16
20	71.91	67.24	64.71	53.97
21	71.75	67.13	64.55	53.81
22	71.60	67.02	64.42	53.68
23	71.39	66.83	64.25	53.55
24	71.26	66.69	64.10	53.40
25	71.14	66.54	63.94	53.27
26	70.97	66.38	63.78	53.11
27	70.82	66.20	63.64	53.01
28	70.65	66.08	63.48	52.75
29	70.49	65.87	63.32	52.61
30	70.35	65.73	63.17	52.48
31	70.19	65.54	63.05	52.28
32	70.09	65.38	62.92	52.19
33	69.84	65.20	62.79	52.02
34	69.64	65.04	62.64	51.89
35	69.53	64.93		51.80

[a] Surface tension standard deviation: ± 0.03 mN·m^{-1}.

Table 3. Surface Tension Values of Triton X-100 at Various Concentrations and Temperatures[a]

	c/(mg·L^{-1})				
	0.52	1.03	2.24	3.86	7.83
t/°C	σ/(mN·m^{-1})				
15	62.67	59.06	53.88	47.84	40.72
16	62.58	58.96	53.79	47.75	40.65
17	62.41	58.79	53.63	47.58	40.37
18	62.26	58.64	53.47	47.39	40.12
19	62.12	58.50	53.32	47.24	39.97
20	61.96	58.36	53.18	47.11	39.85
21	61.81	58.21	53.05	46.96	39.72
22	61.66	58.08	52.92	46.83	39.59
23	61.55	57.95	52.79	46.70	39.45
24	61.43	57.83	52.68	46.57	39.31
25	61.30	57.71	52.56	46.44	39.16
26	61.20	57.62	52.45	46.36	39.07
27	61.10	57.52	52.38	46.25	38.97
28	61.01	57.42	52.30	46.18	38.89
29	60.88	57.31	52.21	46.09	38.76
30	60.78	57.19	52.13	46.04	38.64
31	60.70	57.08	52.05	45.93	38.58
32	60.61	56.99	51.97	45.86	38.48
33	60.50	56.92	51.88	45.79	38.41
34	60.42	56.84	51.77	45.73	38.36
35	60.32	56.79	51.70	45.65	38.34

[a] Surface tension standard deviation: ± 0.03 mN·m^{-1}.

face tension seems to be relatively independent of surface concentration beyond 23 °C. Values for the slope B range from −0.179 mN·m^{-1}·K^{-1} to −0.145 mN·m^{-1}·K^{-1}. These values for the temperature sensitivity of surface tension are somewhat greater than that of water, which was determined by Korosi and Kovats[44] to be −0.138 mN·m^{-1}·K^{-1} at 20 °C. The results indicate that there is about a 2.0 % change in σ from the lowest temperature to the highest temperature while increasing the concentration by approximately 4-fold, decreases σ by approximately about 4.0 %.

The surface tension values for hemicyanine determined in the present study differ somewhat from those reported by Vogel and Hirsa[33] at 22 °C. In particular, our low and high concentration data points are in good agreement with their results, but at intermediate concentrations, our surface tension values are somewhat higher than theirs. There is no obvious reason for this difference, except to note again that we used a direct means of determining concentrations as compared to the more indirect method (SHG) used by Vogel and Hirsa. It should be noted that surface contamination, which can result from lack of thorough surface cleaning, can be an important factor as well. This may be one reason that our surface tension values are higher than Vogel and Hirsa's. Overall, the maximum difference between our data and theirs is about 12 %. Figure 3 shows that σ decreases with increasing t showing an overall relative surface tension change of 4 % to 5 %. Unlike oleyl alcohol, by increasing the concentration of hemicyanine by about 4-fold, σ can be reduced by about 25 %. From this perspective, the temperature can be used as a mechanism for fine-tuning the surface tension of the free surface. Here, the resulting dσ/dt values vary from to −0.159 mN·m^{-1}·K^{-1} to −0.149 mN·m^{-1}·K^{-1}.

For Triton X-100, the surface tension values at 25 °C are comparable to those given by De la Maza and Parra[41] and Saylor[36] at 22 °C; the values lie between these two published data sets. The change in surface tension values

Table 4. Surface Tension Values of SDS at Various Concentrations and Temperatures[a]

	c/(mg·L^{-1})			
	6.27	15.7	27.3	33.8
t/°C	σ/(mN·m^{-1})			
15	71.99	65.28	64.13	69.24
16	71.91	65.17	64.05	69.10
17	71.74	65.00	63.88	68.89
18	71.58	64.83	63.72	68.76
19	71.41	64.67	63.56	68.59
20	71.24	64.48	63.37	68.45
21	71.07	64.32	63.19	68.28
22	70.89	64.17	63.02	68.11
23	70.76	64.03	62.88	67.97
24	70.59	63.86	62.74	67.78
25	70.43	63.71	62.60	67.63
26	70.29	63.57	62.49	67.44
27	70.16	63.41	62.36	67.29
28	70.01	63.26	62.25	67.11
29	69.84	63.08	62.11	66.95
30	69.68	62.94	62.01	66.77
31	69.53	62.76	61.90	66.61
32	69.39	62.66	61.83	66.42
33	69.23	62.52	61.72	66.25
34	69.08	62.32	61.62	66.04
35	68.94	62.16	61.54	-

[a] Surface tension standard deviation: ± 0.03 mN·m^{-1}.

Table 5. Linear Fit Parameters Associated with Eq 1

surfactant	Γ (mg·m^{-2})	c (mg·L^{-1})	A (mN·m^{-1})	B (mN·m^{-1}·K^{-1})	R^2 [a]
oleyl alcohol	0.0265		73.4	−0.174	0.999
	0.0398		72.1	−0.180	0.998
	0.0530		70.9	−0.155	0.996
	0.101		70.0	−0.145	0.996
hemicyanine	0.0587		75.1	−0.158	0.999
	0.105		70.5	−0.159	0.999
	0.159		67.7	−0.150	0.999
	0.235		57.0	−0.149	0.999
Triton X-100		0.52	64.4	−0.118	0.991
		1.03	60.7	−0.116	0.991
		2.24	55.4	−0.109	0.985
		3.86	49.3	−0.110	0.977
		7.83	42.3	−0.121	0.974
SDS		6.27	74.4	−0.155	0.999
		15.7	71.8	−0.167	0.999
		27.3	67.6	−0.156	0.999
		33.8	66.1	−0.134	0.989

[a] $R = \overline{[(\sigma-\bar{\sigma})(t-\bar{t})/\sigma_{\mathrm{rms}}t_{\mathrm{rms}}]}$ where $\bar{\sigma}$, $\bar{t}$, σ_{rms}, and t_{rms} are the average surface tension, average temperature, root mean square surface tension, and root mean square temperature, respectively.

over the temperature range considered is on the order of 4 % to 6 %. There is approximately a 35 % decrease in surface tension as the concentration increases by approximately 15-fold. The slopes range from −0.109 mN·m^{-1}·K^{-1} to −0.121 mN·m^{-1}·K^{-1} showing that Triton X-100 is somewhat less sensitive to temperature than the two insoluble surfactants discussed above.

The surface tension data for SDS is within 15 % of the data reported by De la Maza and Parra[41] at 25 °C over the range of concentrations considered. The surface tension decreases by about 4.0 % over the temperature range considered, and by increasing the concentration by about 5-fold, the surface tension decreases about 10 %. The slopes for SDS range from −0.134 mN·m^{-1}·K^{-1} to −0.169 mN·m^{-1}·K^{-1}. These values are in the same range as those for oleyl alcohol and hemicyanine.

The relationship between surface concentration and the slopes (−dσ/dt) are given in Figure 6A,B for the insoluble and soluble surfactants, respectively. It is clear from this figure that there is very little variation in the slopes with respect to concentration. These data lead to the question of whether any standard model for the variation of surface tension with temperature and concentration are useful in describing the data obtained in this investigation. The most elementary model for an ideal insoluble monolayer, which is the analogue of the ideal gas law[29,43] is given by

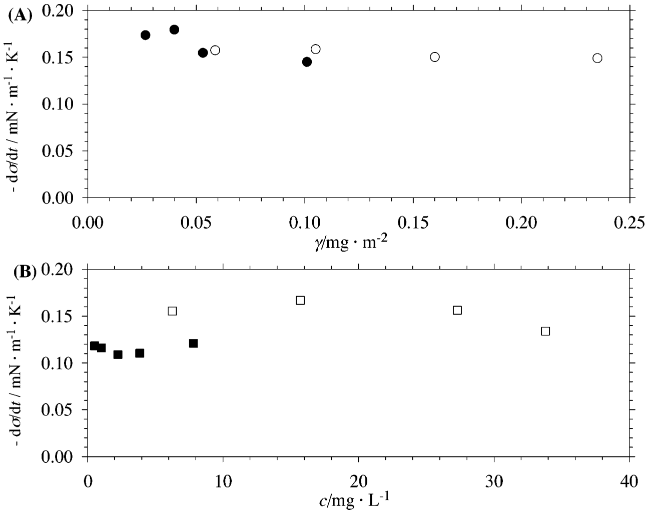

Figure 6. Plots of slope versus concentration for (A) insoluble surfactants: ●, oleyl alcohol; ○, hemicyanine and (B) soluble surfactants: ■, Triton X-100; □, SDS.

$$\sigma = \sigma_{\mathrm{w}} - (R_{\mathrm{g}}/M)\gamma T \tag{2}$$

where σ_{w} is the surface tension of water, R_{g} is the universal gas constant, M is the molecular weight, and T is the absolute temperature. Differentiation of the above gives

$$\mathrm{d}\sigma/\mathrm{d}T = -(R_{\mathrm{g}}/M)\gamma \tag{3}$$

Thus, the model predicts that the sensitivity of the surface tension to changes in temperature should depend linearly on surface concentration for insoluble surfactants. This is clearly not the case for the range of concentrations considered here as indicated by the data in Figure 6A,B.

For the soluble surfactant case, the Gibbs equation[43,45] can be used to determine the slope as follows:

$$\mathrm{d}\sigma/\mathrm{d}T = -\Gamma R_{\mathrm{g}} \ln(c/c_0) \tag{4}$$

where Γ is the excess surface concentration, and c_0 is a reference concentration. This model predicts slopes which vary more slowly with concentration as compared with eq 3. Nevertheless, the lack of any obvious nonconstant functional dependence of the slope on concentration suggests that a more accurate representation of the data may be given by the first few terms in a Taylor series expansion as follows:

$$\sigma = \sigma_0 + \left.\frac{\partial \sigma}{\partial c}\right|_{t=t_0}(c - c_0) + \left.\frac{\partial \sigma}{\partial t}\right|_{c=c_0}(t - t_0) \tag{5}$$

where the subscript 0 refers to reference values of the indicated quantities. This model decouples the concentration dependence from the temperature dependence and is strictly linear in each variable and would therefore appear to bes a more accurate model for the behavior of these surfactants in the concentration and temperature ranges explored in this work. Naturally, higher order nonlinear terms can be added to this expression to improve the accuracy of such models if desired.

Conclusion

This study focused on determining the dependence of the surface tension on temperature over a range of concentrations for soluble and insoluble surfactants that have been widely used in a number of studies involving free surface hydrodynamics. It was found that in the temperature range (15 °C to 35 °C) that the surface tension for hemicyanine, Triton X-100, and SDS decreases linearly with temperature. Oleyl alcohol exhibits such a linear behavior as well up to ≈ 23 °C at which point the surface tension becomes relatively independent of temperature. This linear dependence of surface tension on temperature appears to be virtually independent of concentration, which precludes the use of standard models to describe the data. A linear model in which surface concentration is decoupled from the temperature may better represent the data for the surfactants considered here.

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