Effect of Span-80 in n-Hexadecane on Surface Tensions at High Temperatures

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Abstract

Drop formation and release, spreading and wetting of substrate, etc., are interfacial phenomena that are critical to the performance of many high-speed processes in digital printing and fabrication. In these instances, dynamic surface tension (surface tension as a function of time) in the presence of a surfactant is more important in evaluating the performance of the process than its equilibrium surface tension. It is known that temperature change can cause a change in the adsorption kinetics of ionic and nonionic surfactants at interfaces resulting in a change in equilibrium surface tension measured with temperatures [1-4]. We have recently reported [5] high-temperature measurements (up to 200 °C) of surface tensions using optical imaging of the liquid/gas interface inside a tapered micropipette created within a comparable sized micro-capillary that was heated by coating an electrically conductive, transparent, tin-doped indium oxide (ITO) thin film. This novel method is further used in the current study for: (i) determining high-temperature equilibrium surface tensions of a non-ionic surfactant, Span-80 in n-Hexadecane (up to 160 °C) and comparing the results with those of the pure liquids6 and; (ii) investigating the effects of this surfactant on the dependence of surface tensions on temperature and time when the equilibrium is perturbed by a rapid temperature-change. The interesting aspect of the surfactant selection is that it is not normally surface active at the air/ n-hexadecane interface at room temperatures but is extremely surface active at high temperatures. Results show that, as expected, surface tension decreases as temperature increases and vice-versa. The values determined by optical measurements closely match the values obtained using theory of corresponding states. Also, the time to attain equilibrium is very short (a fraction of a second) and there is hysteresis in dynamic surface tensions between the temperature increase and decrease cycles with the decrease cycle lagging behind the increase cycle. Surfactant concentration is important in affecting dynamic surface tension but does not seem to play a significant role in the reduction of equilibrium surface tensions.

1. Introduction

We know that the time to equilibrium and therefore the dynamic surface tension varies at constant temperature [6-12]. However, in these experiments we are investigating how the dynamic surface tension varies as the temperature is increased or decreased rapidly between room temperature ~ 26 °C and 200 °C. In other words, we are investigating the temperature induced dynamic surface tension (both increasing and decreasing) and explore how surfactant concentration affects this process.

For this system, results indicate that during the temperature increase or decrease cycle, the dynamic surface tension may not change in lock-step with the temperature, and we observe hysteresis. Our video set up with the micro-capillary system makes it uniquely possible to achieve both high-temperature and high-speed measurement [13] of dynamic surface tension. The custom made thermocouple used in these studies has a sensitivity response time to the environment temperature of 0.05 s when exposed to air and 0.002 s in contact with water.

2. Experimental

2.1 Materials

Fast response thermocouple is custom made of purchased unsheathed fine gage microtemp thermocouples (0.001 inches diameter, CHAL-001, Omega, USA) and round boro microcapillary (0.05 inches I.D. × 0.08 inches O.D., CV0508, Fiber Optic Center, USA). Span 80 and n-hexadecane (99%) were purchased from Sigma–Aldrich (St. Louis, Missouri, USA).

2.2 Equilibrium surface tension measurements

Based on the technique discussed in our previous paper [5], we conducted a series of experiments to measure the equilibrium surface tensions of Span 80 in n-Hexadecane solutions with five different concentrations, 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M, and 10^{-2} M from room temperatures up to 160 °C with three repeats for each concentration.

In previous experiments for measuring pure n-hexadecane (boiling point 287 °C), the upper temperature limit was chosen as 200 °C. At such high temperature, pure n-hexadecane becomes too volatile and makes the water/air interface in the capillary system unstable i.e., when heated longer than one minute, the vapors condense on the wall of pipette and the liquid flows back to the interface disturbing it. In this study, the presence of Span 80 surfactant, which has a boiling point of only a little above 100 °C, contributes to a decrease of the boiling point of the surfactant/ n-hexadecane solution compared to that of pure n-hexadecane; therefore the solutions become very volatile at a much lower temperature of 160 °C. Therefore, the highest temperature achieved in the equilibrium studies was limited to 160 °C. The dynamic studies could still go on to 200 °C as the experiments are completed in seconds before vapor effects cause instabilities. The average results of three repeats of equilibrium tensions for each concentration are listed in Table 1.

According to the theory of corresponding states, the magnitude of γ changes almost linearly with temperature within a

Table 1 Average surface tension of Span 80 in n-Hexadecane solutions with 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M, and 10^{-2} M up to 160°C

Temp. (°C) \ Concentrations	10^{-6} M	10^{-5} M	10^{-4} M	10^{-3} M	10^{-2} M
27	29.53	30.03	30.76	29.65	29.76
40	27.56	28.45	29.43	28.16	28.38
60	26.08	25.98	27.65	25.58	26.26
80	23.56	24.73	25.28	23.81	24.30
100	21.56	21.76	22.78	20.88	22.81
120	19.41	19.86	21.03	19.30	20.60
140	17.95	17.95	18.63	17.83	18.75
160	15.65	15.91	17.51	15.91	16.63

relatively narrow range, and has the relation below,

$$\gamma_T = \gamma_0 (1 - k_0 T) \quad (1)$$

Where k_0 and γ_0 are constants and T represents temperature (°C), different liquids have different k_0 and γ_0. Using the above equation, the calculated parameters from data in Table 1 is presented Table 2.

Table 2 Corresponding theory parameters for Span 80 in n-Hexadecane solutions with 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M, 10^{-2} M, and pure n-hexadecane

Systems \ Parameters	γ_0	k_0
10^{-6} M	31.974	0.003203
10^{-5} M	32.596	0.003218
10^{-4} M	33.457	0.003073
10^{-3} M	31.980	0.00323
10^{-2} M	32.170	0.00300
n-Hexadecane	30.344	0.00290

From this table we observe that besides the normal linear decrease in the surface tensions of Span 80 solutions upon the increase of temperature, they also decrease slightly faster than pure n-hexadecane (k_0 contributes to the slope). However for a given temperature, comparing the values between these five different concentrations, there is no observable difference between them. The differences, if any, are possibly due to an intrinsic error of about 5% when using this video microscopic measurement technique.

2.3 Temperature increase induced dynamic surface tension measurements

Using the same setup as above, for each of the surfactant concentrations, the temperature was increased from 26 °C (room temperature) to 200 °C within a total time period of only 10s or less by applying a set voltage to the ITO film on the exterior of the micro-capillary suddenly by turning on a pre-set transformer (set to a specific voltage to get required temperature).

In order to determine the dynamic surface tension, the XCAP™ Image Processing Software was used to record real time video of the microcapillary observed by microscope at the rate of 60 frames per second with the corresponding computer clock time for every single image. From analyzing the video images, we make the plot of the surface tension versus time.

To follow surface tension changes with system temperature change we needed to record the temperature change at the same time. Therefore, we set up another high-speed / high-resolution camera to record at 25 frames per second that was fast enough to capture all the temperature refreshes in the digital gauge screen. At the same time when the computer was recording the microscope and showing what was happening on the PC screen with time display, the second camera was also recording both the PC screen and the digital gauge screen. In this way, we were able to plot the temperature profile against time. Thus we have the dynamic surface tension plot as well as its corresponding temperature changing plot. However, a direct comparison of temperature changing profile and surface tension profile is not straight forward and we are unable to judge small differences (in shape) in between. Therefore, we converted the temperature profile to surface tension profile by calculating it through equation $\gamma_T = \gamma_0 (1 - k_0 T)$ to get the corresponding equilibrium surface tension at a specific temperature. In this way, we can compare the dynamic surface tension and the corresponding equilibrium surface tension at a specific time. The obtained data is shown in Figures 1 and 2.

In all graphs of Figure 1 and 2, calculated surface tension means the surface tension calculated from the corresponding theory of states with the parameters shown in Table 2; i.e., in the first plot, solution 10-6 M is used, so the surface tensions are calculated by γ_T=31.974×(1-0.003203T) (mNm-1). The dashed lines represent calculated values corresponding to temperature changes and the solid lines represent dynamic surface tension determined from video analysis; the surface tension decreases as the temperature increases.

In Figure 1, each image (a through e) shows three repeats of calculated and measured surface tensions for each Span-80 concentration of 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M, and 10^{-2} M, respectively. To look for any trends, Figure 2 was derived with the averages of the three calculated and measured surface tensions for each concentration from Figure 1 by linear interpolation. It is important to note that since all three (repeat) experiments at each concentration are not completed at an exactly same length of time, it is necessary to extend each interpolation to the same length of time. To do this, we chose the longest time among all the data (calculated and measured) at each concentration since surface tensions for the two other repeats would have reached the equilibrium and both the system temperature and surface tension do not change during the extended time. Thus, at each concentration in Figure 1 we get two averages, measured and calculated. All ten averages are shown together in Figure 2.

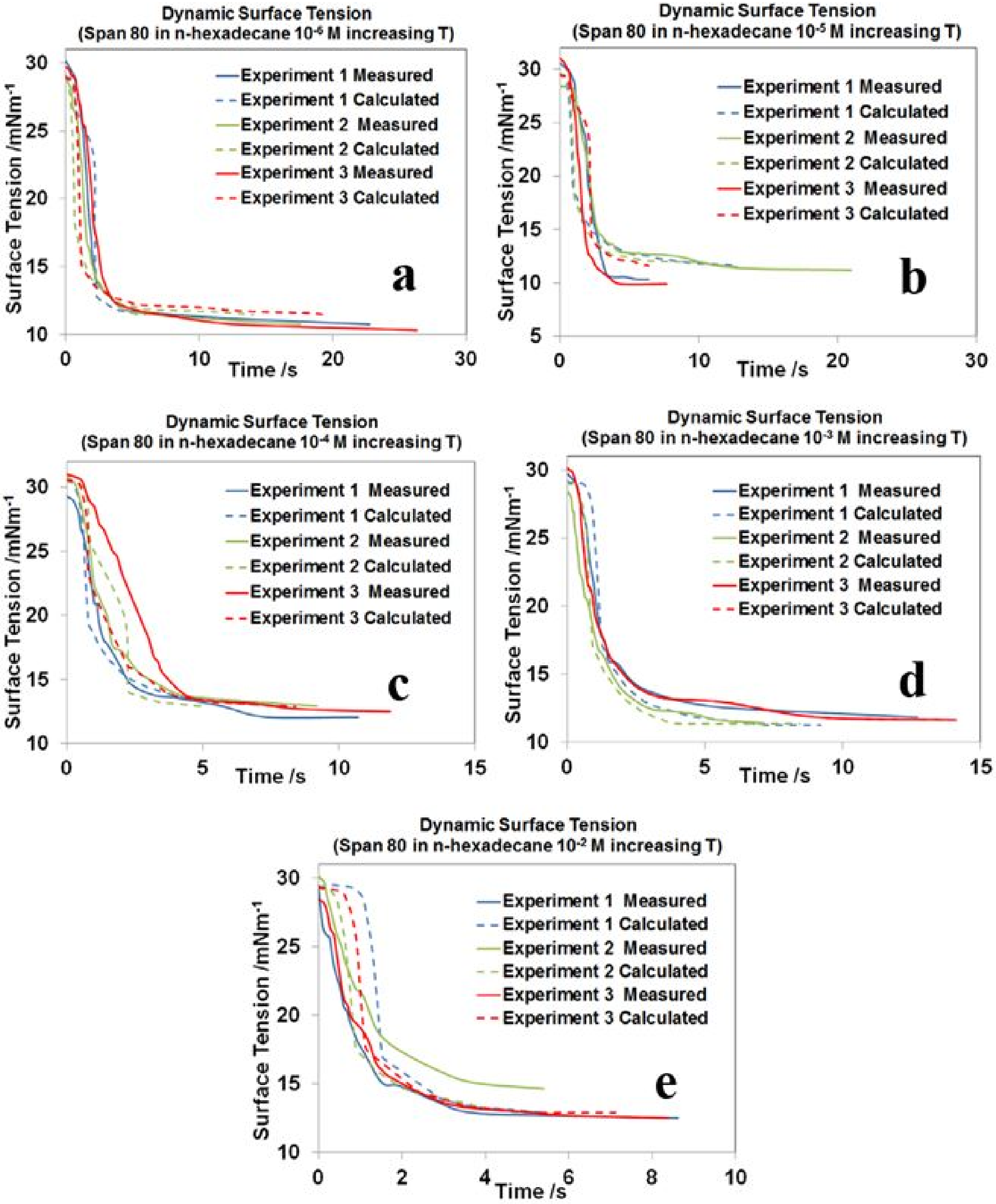

Figure 1 *Dynamic surface tensions of Span 80 in n-Hexadecane solutions with* 10^{-6} *M,* 10^{-5} *M,* 10^{-4} *M,* 10^{-3} *M, and* 10^{-2} *M in the temperature-increase cycle.*

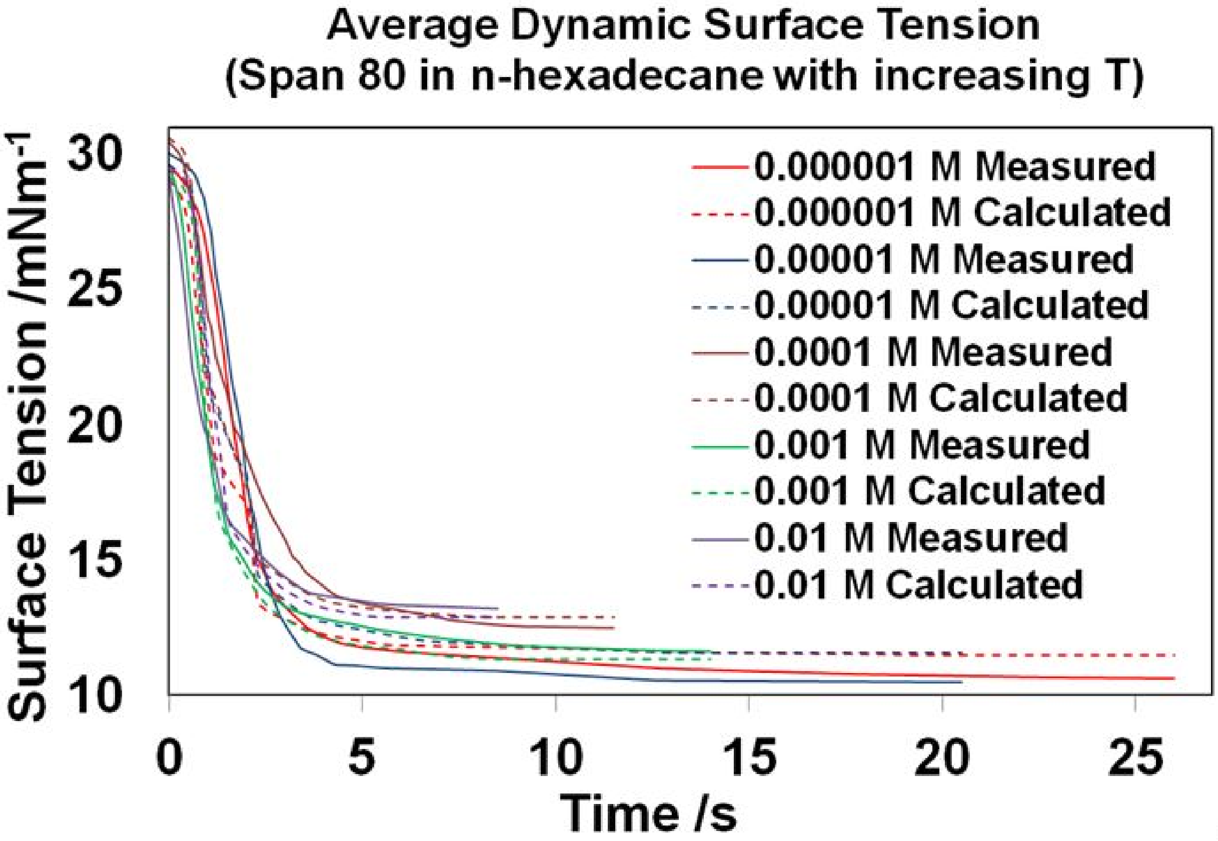

Figure 2 *Average plots of measured and calculated data of Experiments 1-3 at various concentrations.*

From these graphs, it is seen that the dynamic surface tension can decrease to almost 16mN/m (at measured temperature close to 200 °C) quickly (within 5 s) and then approaches equilibrium. Also, from Figure 2, it is seen that the dynamic surface tensions do not show any dependence on Span-80 concentration. In this time scale (several seconds), despite the extremely fast rate of increase in temperature, there is also a synchronized decrease of surface tension to the changing temperature.

2.4 Temperature decrease induced dynamic surface tension measurements

The same set up was used in experiments with decreasing temperature as well. The dynamic surface tension is determined when the applied voltage to heat the micro-capillary is shut-off and the temperature decreases from 200 °C back to 26 °C (room temperature) quickly due to natural convection heat transfer to the environment. The temperature decrease has an initial rate of 100~130 °C/s and then approaches to 26 °C within only about 30s in total.

The following graphs, Figure 3 and Figure 4, show the dynamic data obtained for the systems studied and they are shown in the same sequence as in the above section.

The curves in Figure 3 show that the increase in calculated surface tension (but not the measured surface tension) with time due to decreasing temperature has much better reproducibility. That is, as seen from all the plots of temperature decreasing experiments, the repeats of temperature converted surface tension profiles (dashed lines) in each figure are almost overlapping and thus have much better reproducibility than increasing temperature experiments. This enables us to make more clear comparison of the dashed lines and solid lines. In general, the increase in surface tension due to a temperature decrease lags behind when compared with the surface tension decrease in the increasing temperature cycle.

For the higher concentration solutions, 10^{-2} M and 10^{-3} M the optically measured and calculated plots are the closest. The 10^{-3} M solution reaches the final equilibrium within 10 s and almost at the same time as system temperature cools down back to room temperature, while the 10^{-2} M solution took about 5 s. In terms of the intermediate concentrations, 10^{-4} M and 10^{-5} M, have the largest differences with significant variation. Although in Experiment 3 for 10^{-5} M and Experiment 2 for 10^{-4} M, the optically determined surface tensions profiles are close to the calculated profiles (from temperature), there is still a lot of variation. The higher concentrations exhibit a closer match. In other experiments, especially Experiment 1, 2 for 10^{-5} M and Experiment 3 for 10^{-4} M the surface tension lags behind significantly and it took total of about 20 s to reach equilibrium. For the lowest concentration, 10^{-6} M, the behavior was in between.

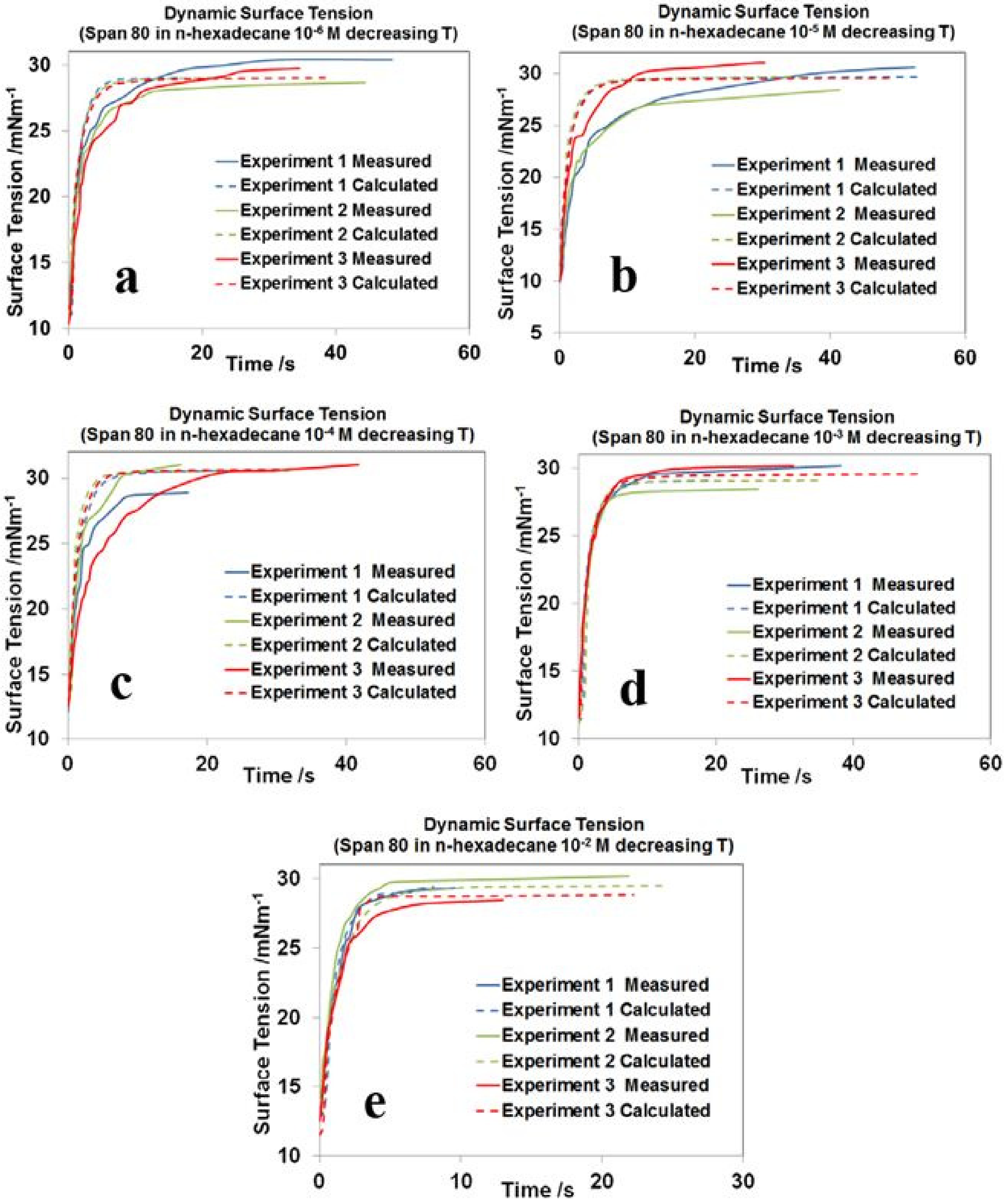

Figure 3 *Dynamic surface tensions of Span 80 in n-Hexadecane solutions a* 10^{-6} *M,* 10^{-5} *M,* 10^{-4} *M,* 10^{-3} *M, and* 10^{-2} *M in the temperature-decrease cycle.*

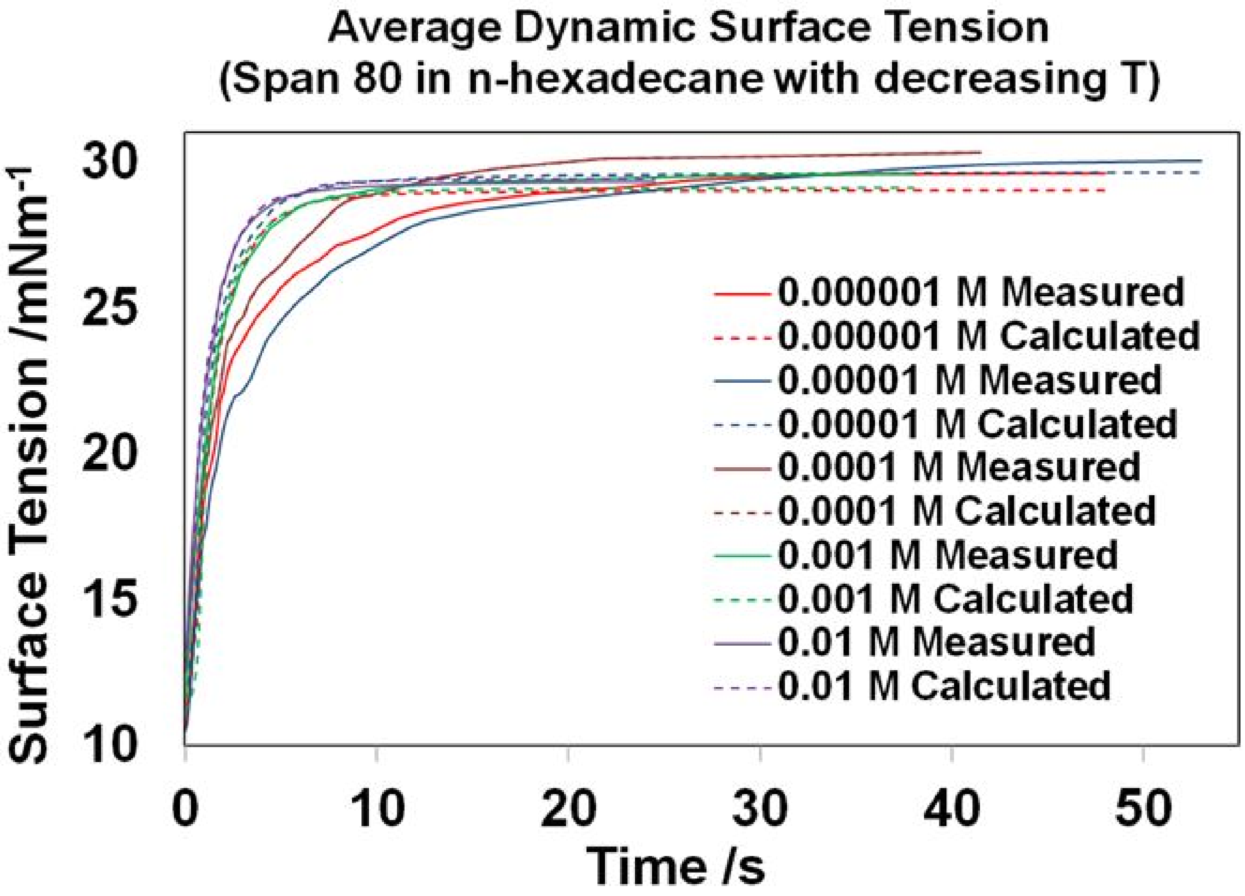

Figure 4 Average plots measured and calculated data of Experiments 1-3 at various concentrations.

In Figure 4, as before, all curves are averages of their corresponding plots of three repeats in Figure 3. Interestingly, these results are very different from the temperature increase induced dynamic surface tension experiments of Figure 2, in that the measured dynamic surface tension increases slower than calculated and thus slower than (lags behind) its corresponding temperature decrease.

3.0 Conclusions

These studies have demonstrated the capability of measuring high temperature induced dynamic surface tension with the resistive heating approach described in our previous work [5]. The technique was applied to study Span 80 in n-hexadecane system with five different concentrations. The rapid temperature-increase cycle induced a dynamic surface tension decrease as the system was heated to 200 °C from room temperature (26 °C) within a total time span of only 10 s while the rapid temperature-decrease cycle induced dynamic surface tension experiments started at 200 °C and had an initial temperature drop of 100~130 °C/s and then approached 26 °C at a slower rate (within about 30s in total). In temperature-increase experiments, all solutions have very fast response to temperature change and reach equilibrium within around 5 s. In temperature-decrease experiments, we found different dynamic surface tension behavior for the five surfactant concentrations. At high concentrations of 10^{-2} M and 10^{-3} M, the dynamic surface tension responses are the fastest, the lowest concentration 10^{-6} M has an intermediate response speed, and the 10^{-4} M and 10^{-5} M solutions have the slowest increase in surface tension. In general, the measured dynamic surface tension increases slower than calculated and thus slower than (lags behind) its corresponding temperature decrease.

Acknowledgements

We gratefully acknowledge support from the Xerox Foundation through the University Affairs Committee (Grant No. HE-1626-2011) and; the Gulf of Mexico Research Initiative for funding this study.

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