Dynamic Surface Tension Measurement of Water Surfactant Solutions

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Dynamic surface tension data for the mixture water + 1-octanol and water + 2-ethyl-1-hexanol with an alcohol mass fraction between $1.6 \cdot 10^{-5}$ and 10^{-3} at (20, 40, and 60) °C were measured. The age of the surface was varied between (0.005 and 50) s. A correlation of the data is given. It has been found that the surface tension of water + 2-ethyl-1-hexanol relaxes faster with respect to time than the surface tension of water + 1-octanol. The results are discussed with respect to the use in absorption chillers.

Introduction

Surfactants are often used in absorption chillers to increase mass transfer in absorbers. Mainly, 2-ethyl-1-hexanol or 1-octanol is added in small amounts to the mixture of water as refrigerant and lithium bromide as absorbent. In the literature, it is stated that Marangoni convection is responsible for the improvement of the absorption process due to surfactants.[1] According to this theory, surface tension gradients are changing sign with respect to temperature and solution composition, whereas in water + salt solutions the surface tension increases with increasing salt content and decreases with decreasing temperature under these circumstances in the presence of surfactants. Since the surfactant solubility decreases when salt is added or the solution is cooler, more surfactant will accumulate at the surface, and thus the surface tension will decrease. This leads to the so-called Marangoni instability when water is absorbed: due to local absorption of water, the film becomes thicker and the surface tension increases. Consequently, molecules flow to this region due to different surface tension and the film becomes even thicker until it destabilizes.[2]

However, up to now there are only a few measurements of the surface tension of water + lithium bromide + surfactant available. Furthermore, the results are very inconsistent. Normally static measurements are published. Since often horizontal tube absorbers are used in absorption chillers, the time of exposure for the solution flowing around one tube is less than 0.5 s.[3] Consequently, it is necessary to measure the dynamic surface tension, i.e., the change in surface tension with time due to relaxation processes. However, in the same way as for the measurements of the static surface tension, the gained data are inconsistent, and interpretations are controversial.[4] Furthermore, all measurements of dynamic surface tension have been obtained at room temperature, whereas absorption in application occurs at elevated temperatures.

To understand the ternary system water + lithium bromide + surfactant, we think it is necessary to gather data of the dynamic surface tension of the binary system water + surfactant first. We present measurements of the dynamic surface tension of water + 2-ethyl-1-hexanol and water + 1-octanol in the range for a surface age of $t = (0.005 \text{ to } 50)$ s at $\theta = (20, 40, \text{and } 60)$ °C and a mass fraction w of $(16 \text{ up to } 1000) \cdot 10^{-6}$.

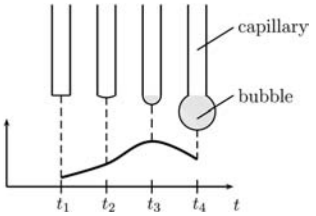

Figure 1. Bubble pressure as a function of the bubble radius and time, respectively.

Experimental Section

The instrument is a bubble tension tensiometer BP2 manufactured by Krüss. For the measurement, a capillary is dipped into a sample of the water + surfactant solution. When inert gas is flowing through the capillary, a bubble is formed immersed at the end of the capillary (Figure 1 at t_1 and t_2). With the Young−Laplace equation

$$\Delta p = 2\sigma / R \tag{1}$$

the interfacial tension can be calculated, where Δp is the pressure difference between the inert gas inside the capillary and the ambient pressure; σ is the interfacial tension; and R is the capillary radius. The pressure inside the capillary is the highest when the bubble's radius is at minimum (t_3). At this point, the bubble is a half sphere, and its radius is equal to the capillary radius. This is the only moment when the radius of the bubble is well determined and, at least in principle, known if the radius of the capillary is known. By measuring Δp at the maximum, the momentary surface tension can be determined. After passing this point, the radius increases again (t_4), and the bubble is finally detached and the next bubble forms.

Depending on the flow rate of the inert gas, the time until the bubble is spherical can be varied. Consequently, the surface age in the moment of determining the surface tension can be varied as well.

The tensiometer is partially encapsulated; i.e., the tensiometer is not gas proof, but it is in a closed cabinet. In spite of the very low vapor pressure of the used surfactants, an increasing surface tension can be observed when the measurement is repeated with the same sample, which is due to evaporation of

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10.1021/je900080a CCC: $40.75

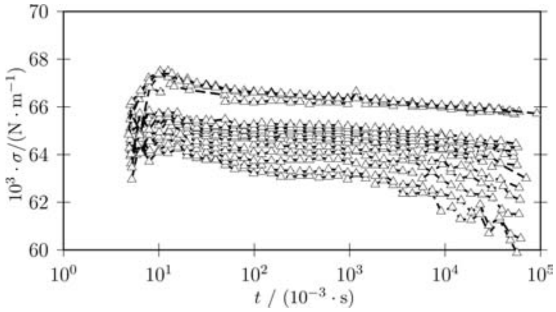

Figure 2. Drift of the surface tension from measurement to measurement for $w = 82 \cdot 10^{-6}$ 1-octanol at 60 °C.

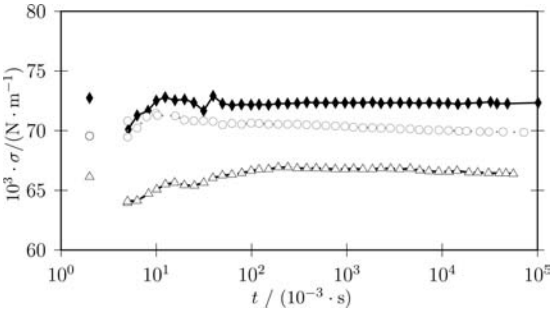

Figure 3. Surface tension for pure water: −◆−, $\theta = 20$ °C; ··○··, $\theta = 40$ °C; - -△- -, $\theta = 60$ °C. The single dots on the left side represent the static surface tension according to Teitelbaum's equation.

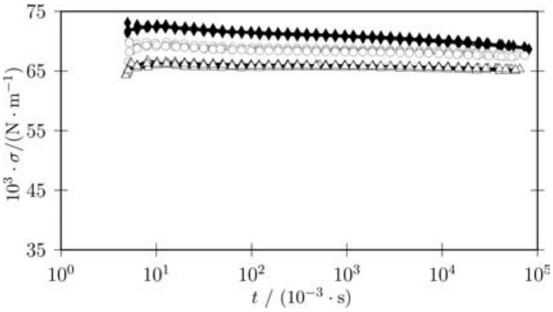

Figure 4. Surface tension for water + $w = 16 \cdot 10^{-6}$ 1-octanol: −◆−, $\theta = 20$ °C; ··○··, $\theta = 40$ °C; - -△- -, $\theta = 60$ °C.

the surfactant. In Figure 2, the long time drift can be observed. Time scale of a measurement is between (0.005 and 50) s. However, the method relies on the assumption that the sample does not change within this time. This may not be the case as shown in Figure 2. The seemingly scattered data originate from several rows of measurements. Each curve starts with a high gas flow and consequently a very short surface age. The surface tension rises sharply, shows a maximum, and flattens off. The lowest curve is the first set of measurements, the highest the last one. Between the beginning of two sets of measurements between (30 and 45) min elapsed, the last two sets were taken 8 h after the foregoing measurement. To circumvent the obvious change of the sample, a small quantity of liquid surfactant was added into the encapsulated room, thereby the environment became saturated with surfactant vapor. Consequently, the surfactant did not evaporate from the solution anymore, and no trend in surface tension from one set of measurements to the next with the same sample could be observed, i.e., only the scatter of measurement uncertainty.

For each temperature, which was maintained by a thermostat (Julabo F32-MC), and surfactant mass fraction, four measurements were conducted. First, the water + surfactant solution was prepared and filled into a closed bottle. Consequently, no surfactant could evaporate from the solution to the environment. The temperature of the bottle was controlled by the thermostat as well. Afterward, a sample of the solution was taken from the bottle, and the surface tension was measured twice. Then a second sample from the bottle was taken, and the surface tension again was measured twice. By this way, a new sample was taken for each temperature. One sample was not used more than 2 h in the measurement device or exposed to the atmosphere, respectively. No reproducible changes between the measurements at one temperature and surfactant mass fraction could be observed, even if one sample was used for 4 h. Consequently, sample stability can be assumed.

Results

The experiments were conducted at three different temperatures ($\theta = (20, 40, \text{and } 60)$ °C) with five different surfactant mass fractions for each surfactant ($w = (16, 82, 150, 330, \text{and } 940) \cdot 10^{-6}$ for 1-octanol and $w = (16, 81, 160, 340, \text{and } 1020) \cdot 10^{-6}$ for 2-ethyl-1-hexanol) and for pure water. The highest surfactant mass fraction is above the solubility limit, so that surfactant islands on the solution's surface could be observed. The raw data can be downloaded as Supporting Information (see below).

The uncertainty of the temperature measurement is 0.3 K, whereas the stability of the used thermostat is in the same range, so that the total uncertainty of the temperature θ is 0.6 K at maximum. The uncertainty of the surfactant's mass fraction w is approximately $10 \cdot 10^{-6}$.

As discussed by Mysels,[5] due to viscous effects, the uncertainty of the bubble pressure method is high at very low surface ages so that we have to disregard some obvious outliers.

For higher surface ages (more than $t = 0.01$ s), we estimated a relative uncertainty in surface tension of approximately 0.5 % (or less than $0.5 \cdot 10^{-3}\ \mathrm{N \cdot m^{-1}}$ absolute). This deviation can also be found within published surface tension data of pure water at room temperature as compared by Gaonkar and Neuman.[6] Our results, together with the values calculated by Teitelbaum's equation[7] for pure water

$$\sigma = (75.69 - 0.1413 \cdot \theta/\text{°C} - 0.0002985 \cdot \theta^2/\text{°C}^2) \cdot 10^{-3}\ \mathrm{N \cdot m^{-1}} \tag{2}$$

(solitary points on the left) are displayed in Figure 3. Oscillations for very low surface ages can be attributed to measurement uncertainty. The agreement between our data and the data according to Teitelbaum is quite good. It is obvious that the dynamic effect is rather small.

Figure 4 displays the surface tension of water + $w = 16 \cdot 10^{-6}$ 1-octanol. The data do not differ much from pure water especially for 60 °C. Note that the scale has been changed to compare the following figures more easily. As expected, the surface tension decreases with increasing temperature.

This changes with increasing surfactant content as for $w = 82 \cdot 10^{-6}$ 1-octanol in Figure 5. It can be observed that the curves for the different temperatures are crossing. This is a consequence of the different solubility of this surfactant in water which increases with increasing temperature. Consequently, the surfactant tends to accumulate less at the surface and will be solved in the solution's bulk. Thus, more water is present at the gas/water interface, and the surface tension is higher. In other words, the sign of surface tension gradient with respect to temperature changes as described above. This effect is often described[2] but not substantiated by experiments up to this date.

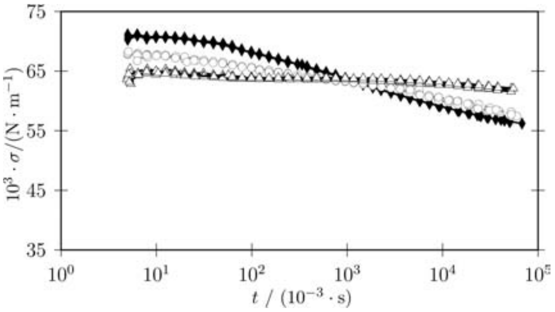

Figure 5. Surface tension for water + $w = 82 \cdot 10^{-6}$ 1-octanol: −◆−, $\theta =$ 20 °C; ••○••, $\theta = 40$ °C; - -△- -, $\theta = 60$ °C.

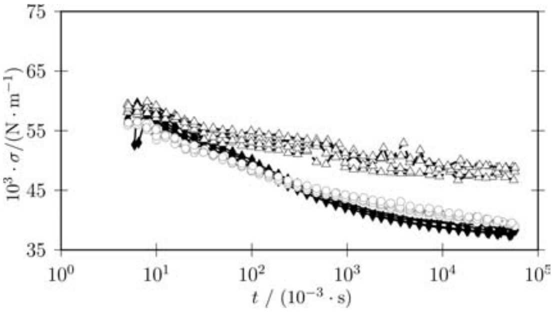

Figure 6. Surface tension for water + $w = 330 \cdot 10^{-6}$ 1-octanol: −◆−, θ = 20 °C; ••○••, $\theta = 40$ °C; - -△- -, $\theta = 60$ °C.

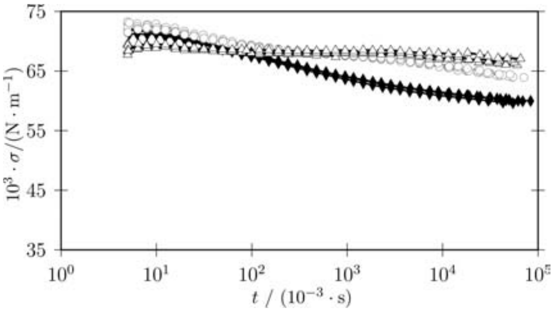

Figure 7. Surface tension for water + $w = 81 \cdot 10^{-6}$ 2-ethyl-1-hexanol: −◆−, $\theta = 20$ °C; ••○••, $\theta = 40$ °C; - -△- -, $\theta = 60$ °C.

It can be concluded that the surface tension of water + surfactant mixtures can increase with increasing temperature, but this is very much dependent on the time scale. At a content of 1-octanol of $w = 82 \cdot 10^{-6}$, this effect can be observed at surface ages higher than approximately 1 s, much too high to be observed in horizontal tube heat exchangers as used in absorption chillers. The new surface will be destroyed by drop formation in a shorter time.

The surface age at which the curves are crossing is decreasing with increasing surfactant content, and the surface tension in general is lower (Figure 6). It also can be observed that the scatter is increasing: To prevent solution from entering the capillary and reducing the free diameter, the capillary is hydrophobic. Since at $w = 330 \cdot 10^{-6}$ 1-octanol there is more hydrophobic surfactant, liquid is entering the capillary and causes the scatter. Obviously, much more outliers have to be removed for analyses.

The surface tension data for 2-ethyl-1-hexanol show the same trend as for 1-octanol. Also, the absolute values are similar. There is a discrepancy at a mass fraction of $w = 81 \cdot 10^{-6}$ 2-ethyl-1-hexanol. As can be seen in Figure 7, the surface age at which the different curves are crossing is shifted considerably to a smaller value compared to 1-octanol in Figure 5. Since the relaxation process is much quicker for 2-ethyl-1-hexanol, it may be concluded that this surfactant is more efficient as an additive in absorption chillers and is consequently more often used.[8]

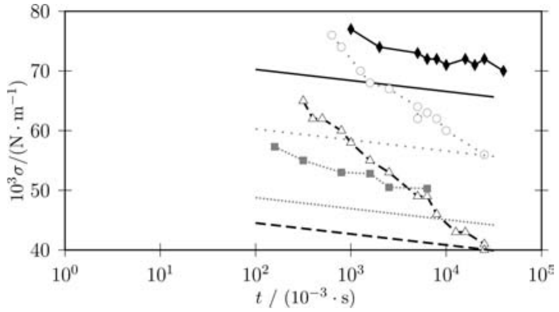

Figure 8. Surface tension data of water + 2-ethyl-1-hexanol mixtures of other sources: −◆− [$\theta = 24$ °C, $w = 0 \cdot 10^{-6}$];[12] −, [$\theta = 24$ °C, $w = 0 \cdot 10^{-6}$] according to eq 4; ••○••, [$\theta = 24$ °C, $w = 190 \cdot 10^{-6}$];[12] • • • • •, [$\theta = 24$ °C, $w = 190 \cdot 10^{-6}$] according to eq 4; - -△- -, [$\theta = 24$ °C, $w = 700 \cdot 10^{-6}$];[12] - - -, [$\theta = 24$ °C, $w = 700 \cdot 10^{-6}$] according to eq 4; ••••□••••, [$\theta = 25$ °C, $w = 500 \cdot 10^{-6}$];[10]•••••••, [$\theta = 25$ °C, $w = 500 \cdot 10^{-6}$] according to eq 4.

Correlation of the Data and Discussion

A comparison of dynamic surface tension data in the literature, which all have been gained at room temperature, shows huge deviations: Luckenheimer, Serrien, and Joos[9] observed a pronounced dynamic effect for water + $w = 12 \cdot 10^{-6}$ 1-octanol. Similarly, Kim and Janule[10] observed also different surface tension data of water + 2-ethyl-hexanol mixtures, whereas their dependency on the surface age is approximately in the same range as in this study (see Figure 8). Vemuri, Kim, and Kang[11] also observed more pronounced dynamic effects of the surface tension of water with 2-ethyl-1-hexanol. Unfortunately, the authors did not publish a value of their surfactant mass fraction. The values of the surface tension of Yuan and Herold[12] for the mixture water + 2-ethyl-1-hexanol are higher than compared to this study. Also, their data for pure water are higher than data published in the literature,[6] and their dynamic effect is more pronounced.

For the mixture water + 1-octanol, a regression analysis was conducted. The resulting equation from the measurements without outliers is

$$\sigma = (79.1 - 1.25 \ln(t/(10^{-3} \cdot \mathrm{s})) - 0.21 \cdot \theta/{}^{\circ}\mathrm{C} + 0.0033 \cdot \theta^2/{}^{\circ}\mathrm{C}^2 - 88 \cdot 10^3 \cdot w + 59 \cdot 10^6 \cdot w^2) \cdot 10^{-3}\ \mathrm{N \cdot m^{-1}} \quad (3)$$

with a regression coefficient of 0.90 and a standard deviation of $3.5 \cdot 10^{-3}\ \mathrm{N \cdot m^{-1}}$.

For the mixture water + 2-ethyl-1-hexanol, we obtain

$$\sigma = (75.8 - 0.80 \ln(t/(10^{-3} \cdot \mathrm{s})) - 0.14 \cdot \theta/{}^{\circ}\mathrm{C} + 0.0024 \cdot \theta^2/{}^{\circ}\mathrm{C}^2 - 57 \cdot 10^3 \cdot w + 31 \cdot 10^6 \cdot w^2) \cdot 10^{-3}\ \mathrm{N \cdot m^{-1}} \quad (4)$$

with a regression coefficient of 0.92. Both sets of data are different at a significance level of 0.95 and a standard deviation of $2.8 \cdot 10^{-3}\ \mathrm{N \cdot m^{-1}}$.

Conclusions

The dynamic surface tension of water + 1-octanol and water + 2-ethyl-1-hexanol solutions has been measured at different surfactant mass fractions and temperatures. It can be concluded that both surfactants decrease the surface tension of water. The relaxation process of the water + 2-ethyl-1-hexanol mixture is more rapid, and thus this surfactant will be more efficient in inducing Marangoni convection.

To reduce the surface tension in the time interval, which is relevant for absorption processes, a certain amount of surfactant is necessary. The minimum amount is dependent on the solution's temperature and the surfactant itself. It has been shown that a higher amount of both surfactants is necessary to decrease the surface tension at elevated temperatures due to an increased solubility limit.

Supporting Information Available:

The raw data of the described measurements can be downloaded as an.xls file. The file consists of one sheet for each surfactant mass fraction. Each sheet consists of three tables, one for each temperature. In the table the surface age and the corresponding surface tension are saved. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review February 15, 2009. Accepted June 8, 2009. This work was supported by the state of Berlin via the NaFöG commission and by the Erasmus programme of the EU.

JE900080A