Dependence of the surfactant solutions surface tension on the concentration and on the temperature

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Abstract. This paper presents the dependence of the surface tension on the surfactant concentration and on the temperature for anionic cetyltrimethylammonium bromide (CTAB) with a concentration of 1 mmol/L and two-ionic lauryl hydroxysultaine (LHS) with a concentration of 2.8 mmol/L. At a low concentration of the surfactant, the surface tension drops sharply at a certain temperature, and at a high concentration it changes slightly, much slower than surface tension of the pure water. Surface tension rapidly drops because micelles in the bulk become unstable and surfactant particles relocate to the interface.

1. Introduction
Modern technologies make it possible to fit active elements, for example, processor cores, in a small area and at the same time increase the number of operations per second. Such a load causes serious heating of equipment in a small area. Existing methods, like fan cooling or radiators require a lot of energy and low ambient temperature. To remove large heat fluxes from a small area, it is necessary to create fundamentally new cooling systems.

Now the most effective cooling methods are evaporation of thin films of liquid, boiling in microchannels and spray cooling \cite{1,2}. The main limitations of these methods, leading to overheating: formation of dry spots \cite{3}, clogging of the microchannel with steam bubbles \cite{4} and uneven heat dissipation \cite{5}. To prevent the crisis of heat transfer, it is necessary to reduce or reverse the thermocapillary effects that lead to Marangoni flow and liquid film rupture \cite{6} and, during boiling in the microchannel, to decrease the size of the boiling bubbles.

To solve these problems, special fluids or additives are used, the most common of which are surface-active substances (surfactants) \cite{7}. They reduce the surface tension of the liquid and improve the wettability of surfaces \cite{8}. In addition, the temperature dependence of the surface tension may become weaker \cite{9}.

Despite the relevance and abundance of articles on measuring the surface tension of pure liquids, there are very few scientific works on measuring surface tension at different temperatures for surfactant solutions. Therefore, the author conducted an experimental study of this dependence.

2. Methods
To measure the contact angle of the surfactant solution on polished annealed copper, we used the KRUSS Drop Shape Analyzer – DSA100. A drop of liquid is placed on a substrate and the firmware
measures the contact angles at both ends of each individual drop. The results averaged over 10 drops in different places of the plate are shown in table 1.

| Table 1. Contact angle of surfactant solutions on the copper plate. |
|---------------------------------------------------------------|
| Liquid | Pure water | CTAB, 1 mmol/L | LHS, 2.8 mmol/L |
| Contact angle, ° | 73.04 | 27.43 | 13.69 |

Both surfactants are ionic; therefore, charged particles on the surface of the liquid interact with the metal substrate and the contact angle decreases.

Surface tension was measured using a KRUSS Force Tensiometer – K100 using the movable plate method. The temperature itself in the tensiometer chamber, in which the sample is placed, is regulated by the temperature of the water in an external thermostat. Since, due to losses, the temperature of the investigated liquid differs from the temperature of the water in the thermostat, the temperature in the tensiometer chamber is measured by a thermistor. For each value of the surface tension, at least 10-20 experiments were carried out so that the root-mean-square deviation from the mean was less than 0.1 mN/m. The author conducted such experiments for each liquid in the range of 25-95 °C in steps of 5 °C.

3. Results
At the room temperature surface tension drops as concentration increases (figure 1). After critical concentration, called critical micelle concentration (CMS), tension reaches minimum and remain constant.

![Figure 1. Surface tension σ vs concentration C at 23 °C.](image)

The surface tension of the CTAB solution at 25 °C temperature is 37 mN/m and slowly decreases with increasing temperature. Then, at 60 °C, it begins to drop sharply from 33 mN/m to 27 mN/m at 75 °C, after which it slowly decreases again (figure 2).
Figure 2. Surface tension of 1 mmol/L CTAB and 2.8 mmol/L LHS solutions vs temperature.

The surface tension of the LHS solution slowly decreases from 34.5 mN/m at 25 °C to 31.3 mN/m at 93 °C. Such a sharp difference in the behavior of surfactants is associated with a change in their internal structure. At a CTAB concentration of 1 mmol/L, micelles become unstable, and hydrophobic tails are collected on the water surface, but this transition does not occur in a 2.8 mmol/L LHS solution as well as in water (figure 3). Moreover, in LHS mean surface tension gradient is 3.8 times less than in pure water.

Figure 3. Derivative of 1 mmol/L CTAB and 2.8 mmol/L LHS surface tension vs temperature.

The finite analogue of derivative is taken from the previous figure.

On the graph of the dependence of the final analogue of the derivative of surface tension on temperature, the difference is even more noticeable. For example, in water at atmospheric pressure, the maximum derivative is -0.19 mN/(m·°C). At a temperature of 65 degrees, the derivative for the CTAB solution takes on a maximum modulus value of -0.558 mN/(m·°C). This is the point of analogue of the phase transition, when micelles dissolve in water.
4. Conclusions
In surfactant solutions, surface tension depends not only on the concentration of the substance, but also on temperature. Moreover, for different surfactants, these dependences differ radically. At a relatively low concentration, as in the CTAB solution of 1 mmol/L, an analogue of a phase transition occurs when micelles - aggregated particles - become unstable, and all hydrophobic tails are collected on the surface of the liquid. At this temperature, the surface tension gradient becomes many times greater than that in water.

At a high concentration, as in the LHS solution of 2.8 mmol/L, on the contrary, the surface tension weakly decreases with increasing temperature, which will make it possible to use such solutions to intensify heat transfer during evaporation and boiling of a liquid.

Acknowledgments
This work was supported by Russian Foundation for Basic Research (No. 19-58-45041).

References
[1] Gatapova E Ya and Kabov O A 2008 Int. J. Heat and Mass Transfer 51 4797–10
[2] Taylorand G I and Michael D H 1973 J. Fluid Mech. 58 625
[3] López P G, Miksis M J and Bankoff S G 2001 Physics of Fluids 13(6) 1601-1614
[4] Nikolayev V S, Beysens D A, Lagier G L and Hegseth J 2001 Int. J. Heat and Mass Transfer 44(18) 3499-3511
[5] Kim J 2007 J. Heat and Fluid Flow 28(4) 753-767
[6] Ward C A and Duan F 2004 Physical Review E 69(5) 056308
[7] Holmberg K, Jonsson B, Kronberg B and Lindman B 2002 Surfactants and Polymers in Aqueous Solution (Chichester: John Wiley & Sons Ltd.)
[8] Wang X, Venzmer J and Bonaccurso E 2016 Langmuir 32 8322–8328
[9] Ye Z, Zhang F, Han L, Luo P, Yang J and Chen H 2008 Colloids and Surfaces A: Physicochemical and Engineering Aspects 322(1-3) 138-141