11 SURFACE TENSION – DETERMINATION OF THE SURFACE TENSION WITH THE STALAGMOMETER

Theory

Surface tension of liquids
The molecules of liquids attract each other by cohesive forces resulting into small distances between the molecules (on the order of 0.1 nm). Thus the compressibility of liquids is lower than that of gas, while the density is much higher. On the other hand, these cohesive forces are not strong enough to result into the fixed position of molecules that can be seen in solid matter. Liquids do not keep a fixed shape, but adapt the shape of a container. Attractive cohesive forces are short range forces which are based on the electronic interactions. They affect molecules in their close vicinity only (zone of molecular interaction). In the bulk of the liquid, each molecule is attracted equally in all directions by the neighbouring molecules, hence zero net force (Figure 1). However, the molecules at the surface do not have other like molecules on all sides around them and they are pulled inwards the liquid core by non-zero net force. Consequently, they cohere more strongly to those associated with them directly on the surface and form a surface "film". Nevertheless, these surface molecules are in the energetically unfavourable state, which forces liquid to minimize the surface area. The geometrical requirement of smallest surface area at the fixed volume is satisfied by the sphere. It is the reason why the free drops of water form spherical droplets.

Figure 1 Cohesive forces in a case of the molecule at the liquid surface and in the bulk

Surface area increase ($\Delta S$), is balanced out by the increase of energy ($\Delta E$), where:

$$\Delta E = \gamma \Delta S \quad (J)$$  

(1)
The coefficient $\gamma$ defines the surface tension in the units of J m$^2$ = N m$^{-1}$. Each liquid is characterized by its own surface tension, which decreases with an increasing temperature. The energetic definition of the surface tension (equation 1) is not the only way to describe it. We can derive it also from the simple experiment shown in Figure 2. It involves the wire rim with the AB side being able to move, and a soap film spanning the space inside the rim. We can observe that the movable wire AB is being pulled towards the soap film, as its area is shrinking down. There is a force in a plane of soap film acting in a direction perpendicular to the wire. It is called the surface force, and is expressed as:

$$F = 2\gamma l$$  \hspace{1cm} (N)  \hspace{1cm} (2)

where $l$ is the length of AB wire and $\gamma$ is the surface tension. According to this, surface tension is defined as a ratio of surface force to a length of rim that is pulled by this force:

$$\gamma = \frac{F}{2l}$$  \hspace{1cm} (N m$^{-1}$)  \hspace{1cm} (3)

Equation (3) defines the surface tension again in units of N m$^{-1}$.

Figure 2 Soap bubble spanning the space inside the wire rim with a movable side AB

The measurement of the surface tension of liquids using the stalagmometer

Stalagmometer is a glass tube, widened in the middle part (Figure 3). Its volume is calibrated by the scale shown on the tube, or by the top and bottom lines. The bottom part of stalagmometer is modified such that the liquid flowing through its smaller diameter forms drops. The drop of a mass $m$ gets released when its weight $G = mg$ is equal or greater than the surface force at the end of tube:

$$mg = 2\pi r \gamma$$  \hspace{1cm} (4)

Equation (4) suggests, that the surface tension $\sigma$ can be calculated from the known water mass ($m$) and the radius of stalagmometer tube ($r$). However, it was shown experimentally,
that only about 2/3 of the drop volume gets released. In addition, this portion is not constant for all the drops.

**Figure 3** Stalagmometer with a calibrated scale

On the other hand, the ratio of the mass and surface tension is constant for all the liquids:

\[
\frac{m_1}{\gamma_1} = \frac{m_2}{\gamma_2}
\]  

(5)

where \(m_1\) and \(m_2\) are the masses of drop 1 and 2 respectively, and \(\gamma_1\) and \(\gamma_2\) are the surface tensions corresponding to these liquids. If the liquid with known surface tension is used for one of them (e.g. water shown in Table 1), the surface tension of the other liquid can be calculated from the equation:

\[
\gamma = \gamma_{\text{water}} \frac{m}{m_{\text{water}}} \quad (\text{N m}^{-1})
\]  

(6)

It is a good practice to measure the mass of several drops in order to increase the precision of the calculation using the equation (6).

**The determination of the surface tension by the drop-weight method**

**Equipment**

stalagmometer, beaker, tubing with a balloon, weighing bottle with a lid, laboratory scale with the precision of the thousands of gram, distilled water, liquids with the unknown surface tension
Experimental procedure
1. Mount the clean and dry stalagmometer on the vertical stand.
2. Weigh the mass of the empty weighing bottle \( m_0 \).
3. Fill the beaker with distilled water. Mount the tubing with balloon on the top end of stalagmometer. Immerse the bottom end of stalagmometer into water and fill it up, such that the water level is above the wide part of stalagmometer.
4. Remove the balloon and collect 20 water drops into the weighing bottle.
5. Weigh the mass of the weighing bottle with drops \( m_0 + m_{\text{water}} = m_{\text{total}} \) and from this equation determine the mass of 20 drops \( m_{\text{water}} \).
6. Empty the weighing bottle and stalagmometer, dry them and prepare for the next measurement.
7. Repeat steps 2-6 for the other liquids with unknown surface tension. Total mass is equal \( m_0 + m_{\text{liquid}} = m_{\text{total}} \). Determine mass of the drops \( m_{\text{liquid}} \).
8. Write the results of the measurements into the Table 2.
9. Measure the laboratory temperature, find the corresponding water surface tension from the Table 1 and calculate the surface tensions of studied liquids \( \gamma \) according to the equation (6).

Table 1 Water surface tension \( \gamma \) and density \( \rho \) as function of the temperature

<table>
<thead>
<tr>
<th>t (°C)</th>
<th>( \rho_{\text{H2O}} ) (g cm(^{-3}))</th>
<th>( \gamma ) (N m(^{-1}))</th>
<th>t (°C)</th>
<th>( \rho_{\text{H2O}} ) (g cm(^{-3}))</th>
<th>( \gamma ) (N m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.99996</td>
<td>0.07349</td>
<td>21</td>
<td>0.99799</td>
<td>0.07259</td>
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<tr>
<td>16</td>
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<td>0.99777</td>
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<td>0.99754</td>
<td>0.07228</td>
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<td>18</td>
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<td>0.99705</td>
<td>0.07197</td>
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<td>20</td>
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<td>0.07275</td>
<td>26</td>
<td>0.99678</td>
<td>0.07180</td>
</tr>
</tbody>
</table>

Table 2 The determination of the surface tension by the drop-weight method

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( m_0 ) (g)</th>
<th>( m_0 + m_{\text{liquid}} = m_{\text{total}} ) (g)</th>
<th>( m_{\text{liquid}} ) (g)</th>
<th>( \gamma ) (N m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1</td>
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<td>2</td>
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<tr>
<td>3</td>
<td></td>
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</tbody>
</table>
Determination of the surface tension by the drop counting method

There are two marks (lines) on the stalagmometer: the top line above the wide part and the bottom line below it. The volume between these two lines is \( V \), and the liquid, with density \( \rho \) contained in this volume, has a mass \( m \):

\[
m = \rho V \quad \text{(g)}
\]

This volume \( V \) corresponds to \( n \) drops, which are released from the stalagmometer upon the decrease of liquid level from top to bottom line mark. Here, the average mass of one drop is:

\[
\frac{m}{n} = \frac{\rho V}{n}
\]

Substituting the mass \( m \) in the equation (6) with the mass of one drop then yields:

\[
\gamma = \gamma_{\text{water}} \frac{\rho_L n_{\text{water}}}{\rho_{\text{water}} n_L} \quad \text{(N m}^{-1})
\]

where \( n_L \) is the number drops of the liquid and \( n_{\text{water}} \) is the number drops of water.

Equipment
stalagmometer, beaker, tubing with a balloon, weighing bottle with a lid, laboratory scale with the precision of thousands of gram, distilled water, liquids with unknown surface tension.

Experimental procedure
1. Fill the stalagmometer up to the top mark with distilled water.
2. Release the water to the weighing bottle and count how many drops it takes to decrease the water level in stalagmometer down to the bottom mark.
3. Write down the number of drops \( n_{\text{water}} \).
4. Empty and dry the weighing bottle and stalagmometer, and prepare it for the next measurement.
5. Repeat steps 1 – 3 for liquids with the unknown surface tension.
6. Write down the densities of studied liquids according to the notes on bottles, and density of distilled water at the actual laboratory temperature from the Table 3.
7. Using equation (9), calculate the surface tension for all the studied liquids.
8. Draw a diagram $\gamma = f(\rho_{\text{liquid}})$ for both methods to millimetre paper as well as with a computer using MsExcel.

9. Compare the results obtained via the drop-weight method and drop counting method.

### Table 3 The determination of the surface tension by the drop counting method

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Number of drops</th>
<th>$\rho$ (kg m$^{-3}$)</th>
<th>$\gamma$ (N m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

### Conclusion

Assess the surface tension – density plots (straight-line or curve).

### References

2. Edition of Department of Physical Chemistry: Laboratory Practice in Physics for Students of Pharmacy. Faculty of Pharmacy, Comenius University, Bratislava, UK 1991.

### Manual written