COMPARISON OF TWO DIFFERENT METHODS TO MEASURE THE SURFACE TENSION OF A SAMPLE OF PENTADECANE

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Abstract: The importance to get a correct measurement of all variables involved in different metrological processes, takes major importance every day. In order to improve the uncertainty of some processes in metrology of density, the surface tension (ST) arises as the new important one in the uncertainty budget. In density measurements different variables like the properties of the liquids are involved (density, viscosity, compressibility coefficient, and surface tension), especially for the reference materials used for the calibration of hydrometers, and their characterization in density (density calibration). The ST appears in those methods were a suspension wire is hanging from a balance and at the same time is holding a solid (density standard or a mass) which is introduced/immersed into a liquid. This method is usually known as hydrostatic weighing. Nowadays there are diverse methods for the determination of the ST, and various devices to do these measurements based on these methods.

The present work focuses on two methods to measure the ST (Method of rupture and hydrostatic weighing method), whose modifications and adjustments were realized in order to reduce the uncertainties of the resulting values. In this paper the measurement systems and results from both methods for a sample of pentadecane at a constant temperature of 20 ºC are presented and discussed.

1. Introduction.

There are a lot of processes were the correct measurement of the ST is an important issue in order to make correct measurements with low uncertainties, and with this the assessment of the product quality is ensured. The ST also plays a very important role in chemical processes that involves heat, mass and momentum transfer operations[1]. In those different processes various factors like the calibration of the different devices used, the experience of the metrologist, in the case that in the process need to be applied liquids, where physical and chemical properties are related to them, among others are involved and has to be considered. In density metrology the most important physical properties are the density, the viscosity and the compressibility factor as well as the ST.

For the determination of the density of solids or liquids and the hydrometer calibration are used different measurement methods, one of them is the hydrostatic weighing. In this method is used a wire that hangs from a balance and which maintains a solid that could be a solid

density standard (solid with known density) or a solid with unknown density, or a hydrometer to be calibrated. In the last case there is usually used the Cuckow Method [2] for the calibration of the hydrometers. In this method a liquid with known density is required (certified reference material in density), also the ST of the liquid commonly used are required too. Generally data bases are used for different groups of liquids (alcohols, oils, hydrocarbons, etc), and the values are very generals, for example, if there is used an alcohol the recommended ST is 25 mN/m. Nevertheless it is very important to know and to use the correct value of the ST because there can be obtained differences in the order of 0,1 kg/m^3[3] in final density value for one liquid used (let's remember that there was used at least two different liquids in this method).

Due to the ST in liquids another phenomenon called the formation of the meniscus is presented, and it can be watched when a wire or something similar is introduced in the liquid and gets in contact with the liquid surface and with the gas (commonly air). The ST is also the force that makes the formation of the meniscus in the recipients with a liquid possible which is also known as the capillarity effect, see figures 1 and 2. In the figure 2 there can be observed a meniscus formed by normal water on the left side and a meniscus formed by mercury on the right side.

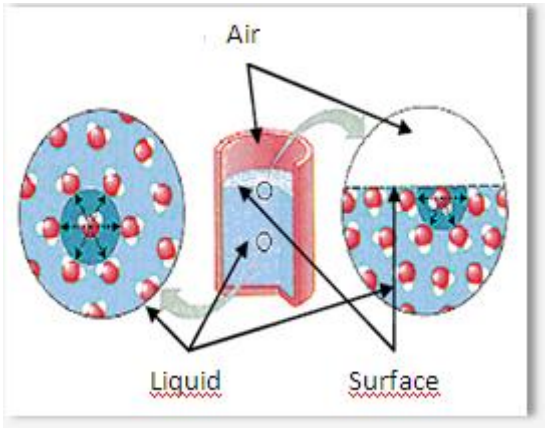

Figure 1. Molecules in the surface and inside of a liquid.

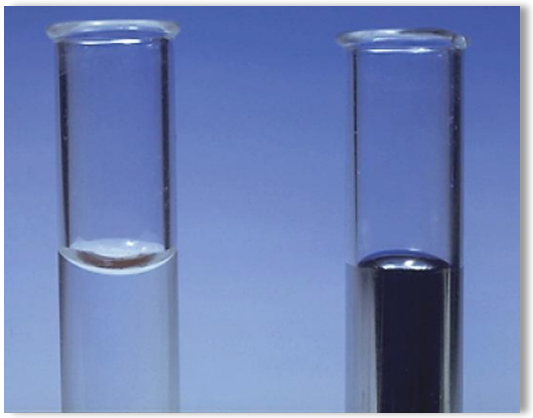
Figure 2. Formation of the meniscus.

The ST is a measurement of the cohesive energy that is presented at an interface (in this case the interface between a liquid and a gas). The molecules of a liquid attract each other in the bottom but this does not occur in the surface of the liquid. Inside the liquid the interactions of all molecules are balanced by an equal attractive and repulsive force in all directions. The molecules on the surface of a liquid experience an imbalance of forces because the force of the molecules is exercised downwards, inside of the liquid and on the other side the force of the molecules in the gas is unappreciable, so the resultant force is the liquid force. In the next picture (figure 3) there is demonstrated how the molecules act in different states.

There are different methods for the measurement of the ST. They are classified, depending on the environment of the system, in static or dynamic ST. This classification occupies other classifications depending on the method for the determination of the ST, like the bubble pressure method[4], the drop shape method[5], the capillary method[6], although some

correlations to predict the ST values depending on the structure of the compounds like the mentioned by Reid et al[7], or the another one proposed by Sastri and Rao[1] are existing.

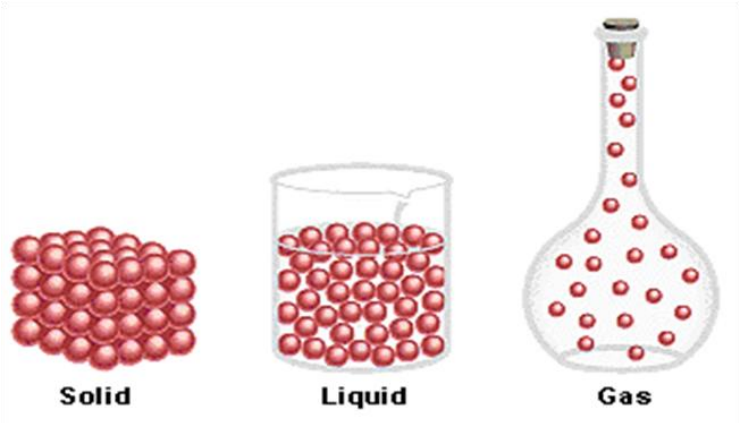

Figure 3. Different distribution of molecules depending of the state of the matter.

In national laboratories like the Centro Nacional de Metrología (CENAM-México) the use of values of properties of the variables involved in the measurement processes is required. The methods that are currently used and from which were performed the current databases offer different values between each other, in the interval of 4 mN/m, in the same liquid, at the same temperature, and even the apparatuses used in industry are based in those methods. For the purpose to reduce these differences and to obtain correct and reliable measurements with a little uncertainty two methods were developed to determinate de ST of liquids at constant temperature.

The first one is the "Hydrostatic weighing method" developed in The Physikalisch-Technische Bundesanstalt (PTB-Germany) and performed at the CENAM facilities which is based on the Archimedes' principle. The second one is the "rupture method", a well known method based on the necessary force to break a small film of liquid between the liquid and a stainless steel ring. Both methods were semi automated and performed for the installations of our primary laboratory.

2. Methodology.

The following two methods presented in this paper were developed in the CENAM laboratories and are presented below.

2.1 The Hydrostatic weighing method.

This method is based on the Archimedes' principle, a principle that states that a body immersed in a fluid is buoyed up by a force equal to the weight of the displaced fluid [8]. A similar work was developed at the PTB by Horst Bettin et al [9]. The method consists in the use of a little stem made of glass and sealed on both sides. The stem has to have a mark approximately in the middle. Furthermore the stem has to be characterized in mass, in volume ($V_T = V_1 + V_2$ were V_1 is one side of the stem from the mark and V_2 the other side), in density and in the diameter at the level of the mark. Then the stem is hanged from a wire under a

balance and immersed into the liquid (with unknown ST) just to the mark. Doing this, there can be observed the formation of the meniscus as shown in the picture below (figure 4).

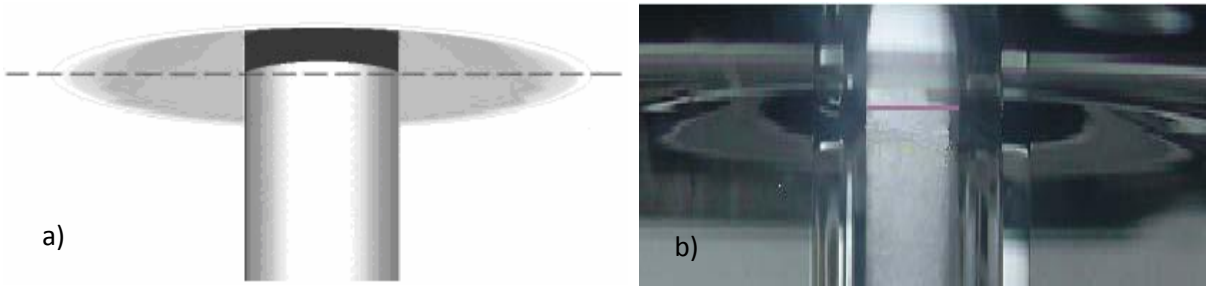

Figure 4. Location and formation of the meniscus.

Then, with the use of a high resolution camera the image is amplified in the part of the meniscus in order to realize a better adjustment of the mark in the horizontal axe of the meniscus. We take the balance indication and make a simple substitution method with standard mass of the same value near to the milligram. The second part of the method is to turn the stem and do the same but with the other side of this (V_2) with the balance indications the ST can be calculated with:

$$\gamma = \frac{(I_1 + I_2) * \left(1 - \frac{\rho_L}{\rho_G}\right) + (\rho_F + \rho_L) * V_T - 2m * g}{2 * \pi * d} \quad (1)$$

Where:
$\gamma =$ Surface Tension
$I_1 =$ Indication of the balance for the first side of the stem
$I_2 =$ Indication of the balance for the second side of the stem
$\rho_L =$ Density of the air at the moment of the measurement
$\rho_G =$ Density of the liquid of unknown ST
$\rho_F =$ Density of the mass standards
$V_T =$ Total volume of the spike
$m =$ Mass of the spike
$d =$ Diameter of the spike
$g =$ Gravity force in the place of the measurement.

2.2 The rupture method.

This measurement method is a mixture of the ring method and the usual rupture method, in the first one the measurement is made with a ring made of platinum which is retired from the liquid, the determination of the ST is calculated from the displacement of the ring before breaking the union by the liquid and the ring. In the rupture method a cylinder for the formation of a meniscus is used and in this case the cylinder is slowly retired from the liquid surface until the separation (rupture) and with this relation the force is measured and directly related with the ST.

So using the principles of the methods mentioned before, a semi automated system using a stainless steel ring hanging from a balance was designed. The ring gets in contact with the liquid surface and the level of the liquid is increased or decreased with a solid that is moved up and down with an engine controlled by an electronic interface. The balance, which is connected with the PC, and its software (developed in CENAM), carries out the continuous reading (and a graph), and accomplishes the calculation in order to show the value of the ST at the moment of the rupture.

In the picture shown below (figure 5) there can be seen the ring during the contact with the liquid and forming the meniscus at the moment that the liquid is diminished, and in the figure 6 the graphic of the rupture moment is shown.

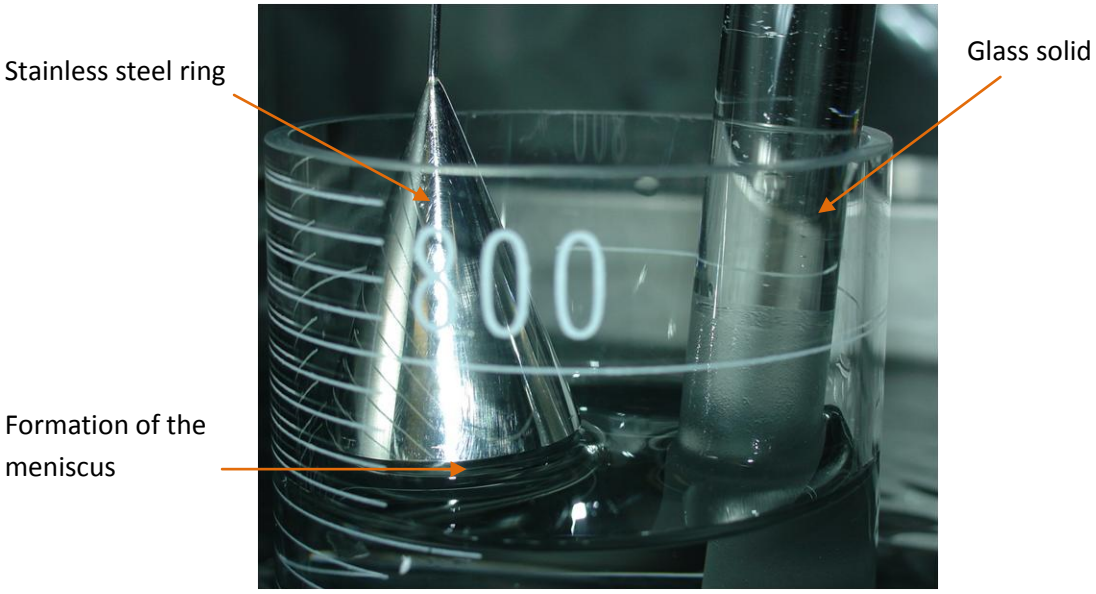

Figure 5. Formation of the meniscus with the ring.

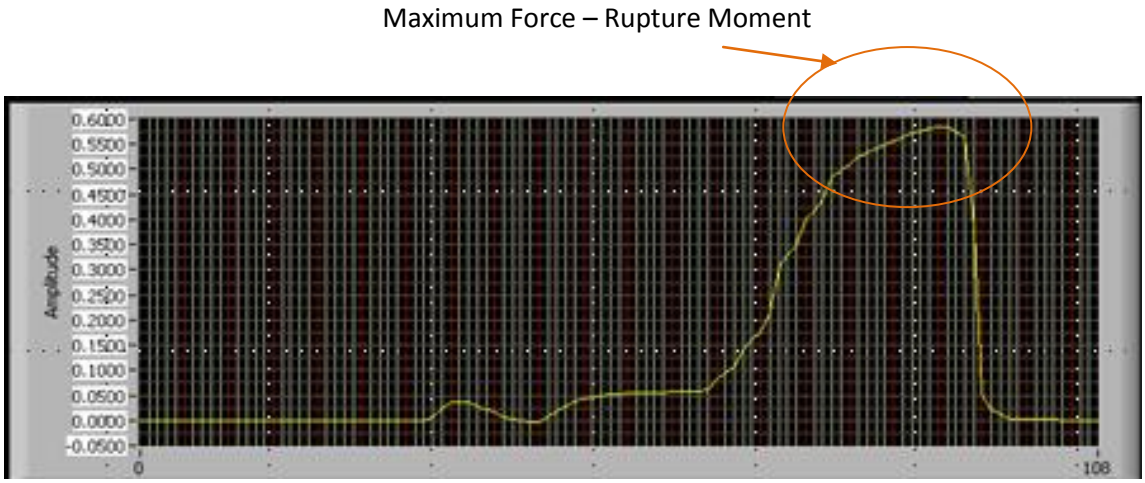

Figure 6. Graphic of the maximum force at the rupture moment.

In this method the ST can be calculated with:

$$\gamma = \frac{(I_b - E_c - R - I_{b2} + E_{c2} + R_2)}{2P} * g * \left(1 - \frac{\rho_a}{\rho_p}\right) \qquad (2)$$

Where:

I_b and I_{b2} = Indication of the balance when the ring in on the maximum tension and suspended on the air respectively.

E_C and E_{C2} = Error of calibration when the ring in on the maximum tension and suspended on the air respectively.

R and R_2 = Resolution of the balance when the ring in on the maximum tension and suspended on the air respectively.

3. Results

Two methods were developed and from both was analyzed a sample of pentadecane which is used as a reference material in the metrology of density. From both was used a thermostatic bath to maintain the control of a constant temperature of 20ºC.

	Surface Tension (ST) mN/m	U Method mN/m	ST WH-ST Rt mN/m	$\sqrt{U_{HW}^2 + U_{Rt}^2}$ mN/m	*En*
Hidrostatic Weighing (HW)	26.58	0.1531	0.5760	0.1591	3.62
Rupture (Rt)	27.15	0.0433			

Table 1. Comparisson of the obtained results.

In the figure 7 the measurements done to the pentadecane by the Hidrostatic Weighing method at 20 ºC are shown. The average value of ST is (26,58 ± 0,016) mN/m with a coverage factor of 95%.

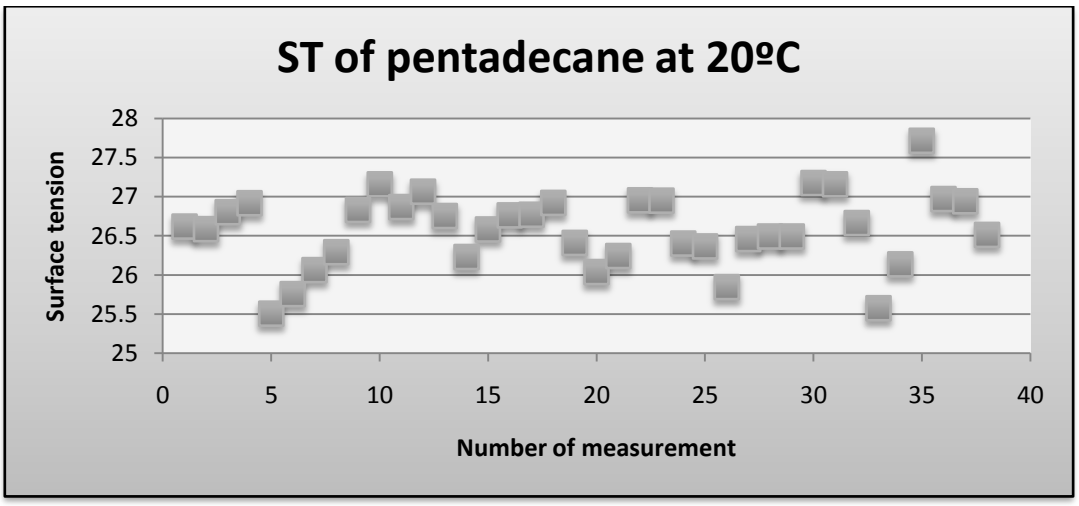

Figure 7. Graphic of the results of ST of the pentadecane by hidrostatic weighing.

In the figure 8 the measurements done to the pentadecane by the Rupture method at 20 ºC are shown. The average value of ST is (27,15 ± 0,04) mN/m with a coverage factor of 95%.

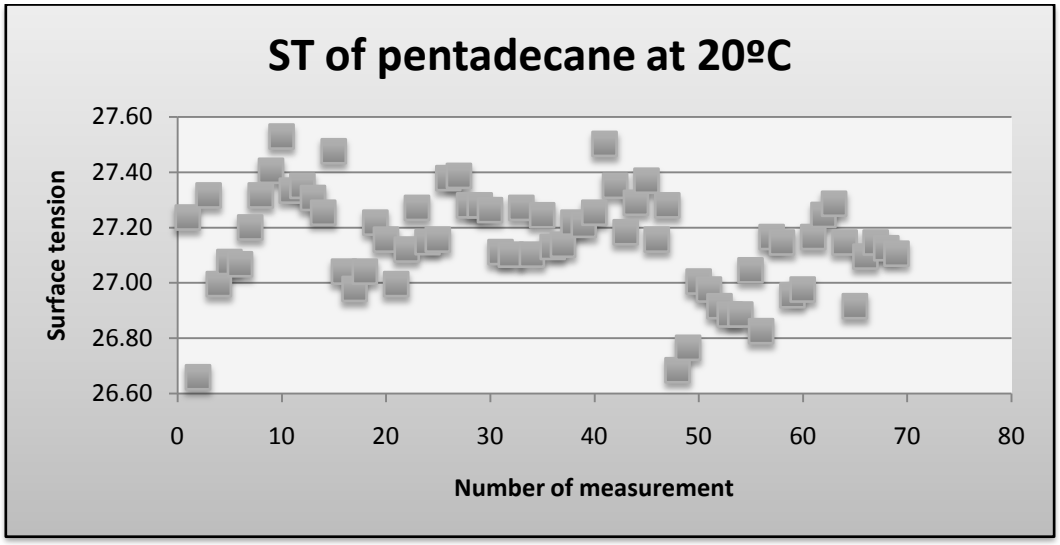

Figure 8. Graphic of the results of ST of the pentadecane by the rupture method.

4. Conclusions

From both methods were obtained good results but each of them has pros and cons and are mentioned below:

Pros:

- Hydrostatic weighing method:
  - The adaptation of the images acquisition used for the location of the meniscus[10].
  - No corrections at the method required.
- The rupture method:
  - The quantity of liquid required for each measurement is 300 mL approximately.
  - The time required for each measurement is 15 minutes.
  - The repeatability of the method is greater than the hydrostatic method.

Cons:

- Hydrostatic weighing method:
  - The time required for a measurement is 6 hours for each one.
  - The quantity of liquid required is 3 L approximately.

- The rupture method:
  - The ring needs to be made of platinum in order to have better contact surface with the liquid.

- Corrections in the formula due to the used ring (different diameter) are required in order to know the volume of liquid after the rupture.

With the results obtained from both methods can be concluded that until the preparation of this report the results between them are not consistent (shown in table 1). The results of the ST values are close to those reported by the PTB (27.17 mN/m) or the estimated by the Macleod-Sudgen [7] correlation (27.23 mN/m) which values are estimated with the structural contibutions of the molecules of the pentadecane and his density. But the results are not suficient in order to choice one as the better method. More measurements have to be made with different liquids and also make some correlations with the chemical structures of the compounds for the improvement of the systems.

This work is the beginning of a bigger research work and we realized that we got a broad experience, furthermore there are a lot of points to be improved in both methods and those are future issues for us.

The author wishes to thanks to Nadine Flachowsky by her contribution.

5. References

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