

A new optical method of continuously analysing the surface properties of a single pendant drop while obtaining quality bulk spectral and refractive index measurements of the liquid-under-test

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Abstract

The classical stalagmometer has been replaced by the tensiometer to measure surface properties from drop volume. From the drop period T_1 , converted into volume, the surface properties of the liquid can be obtained. In the fibre drop analyser the use of the graphical signal (tensiotrace), significantly extends the measurement potential of the tensiometer by providing additional measurands. This instrument produces a series of peaks. The third-order reflection is known as 'the tensiopeak-period' t_3 , and accurately predicts the value of the drop period. The results of an experimental study confirm the relationship between T_1 and t_3 for a wide range of liquids and are supported by ray-tracing modeling. Very sensitive and high quality bulk UV-visible spectra and refractive index measurements can be obtained from the drop-under-test.

1. INTRODUCTION

1.1 Background to Study

The stalagmometer is an instrument for measuring the size of drops suspended from a capillary tube, used in the drop-weight method from which the tensiograph was developed¹. The stalagmometer/tensiometer is an instrument designed to measure the surface tension of a pendant drop determined by drop volume or drop weight measurements. The technique began its evolution from an inauspicious beginning of a proposal by a pharmacist Tate² in 1864 for making up reliable preparations³ of drugs to emerge as a reliable scientific measurement technique through the work of Rayleigh⁴, Harkins and Brown⁵, and Lohnstein⁶ around the turn of the nineteenth century. In recent times Miller and co-workers⁷ led the development of commercial products. McMillan and co-workers have developed the tensiograph technology from this historical platform and in recent studies pointed to the excellent capabilities of the technique for spectral⁸ and other measurements⁹.

1.2 The optical tensiograph instrument and the tensiotrace

The optical tensiograph is an Amplitude Modulated Fibre Optic Sensor (AMFOS) instrument that records a tensiotrace. The tensiotrace is an evolutionary signal recorded from the light coupled between a source and collector fibre as the drop moves through its entire life cycle from a remnant drop to a fully evolved drop that finally detaches from the optrode head. The instrument has been engineered to deliver measurements of the physical properties of the Liquid under Test (LUT), namely

surface tension/density ratio, refractive index (η), colour at a specific wavelength (absorption = A_λ) and turbidity at a specific wavelength. The instrument can also of course be used for quality assurance for solid products such as pharmaceutical products if these are dissolved in an appropriate solvent for this purity/fingerprinting assay. It can also be used to sensitively monitor chemical and biochemical kinematics processes. Tensiography uses optical fibres to illuminate a forming pendant-drop from within with source and collector fibres located in a conventional drophead. Figure 1 shows a typical concave drophead. The actual problem with such a design is fundamental in that physical damage can be caused due to exposure of the fibres. A patented quartz drophead¹⁰ has been designed that gives the same universal fingerprint capability as this traditional drophead. This new design of drophead is one of the key innovations that at last facilitate accurate, reproducible and sensitive tensiography.

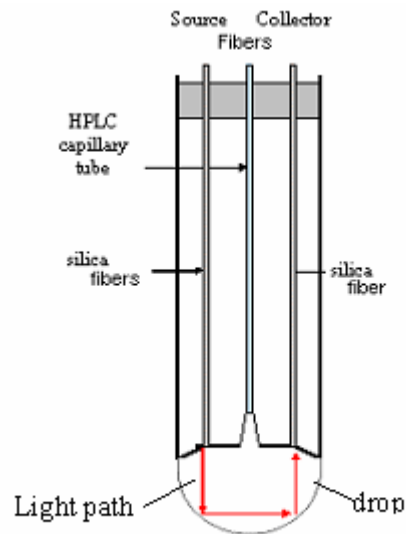
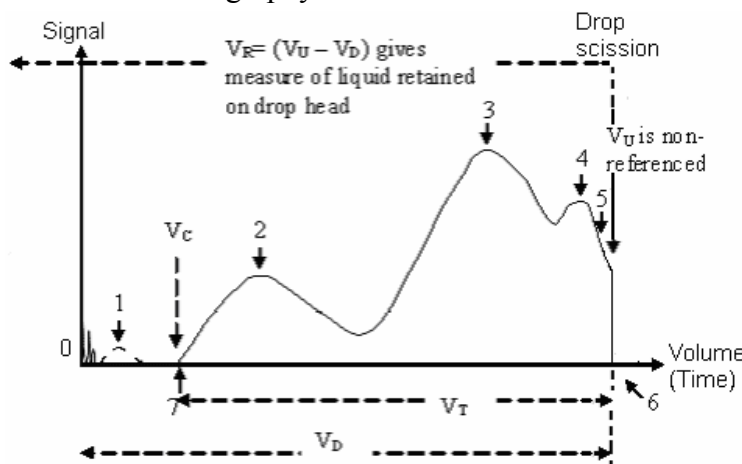


Figure 1: Drophead configuration



Label	Description
0	Separation vibration
1	First-order peak
2	Rainbow peak
3	Tensiopeak
4	Shoulder peak
5	Separation peak
6	Drop period
7	Rainbow peak commencement

Figure 2. Tensiotrace showing the important trace features associated with drop mechanics, labelled 0 to 7.

Figure 2 shows the important features of the tensiotrace. The computer model reveals that the coupling of the light from source fibre to collector fibre can almost be represented as a 2-D process as the drop grows. The light must enter the collector fibre within the acceptance angle. An important measurement position is known as the commencement (7) at which the light from source fibre is received by the collector fibre and can be transmitted in the multimode fibre to the detector. In the drophead design used in this study no light couples to the detector until the second order reflection begins to develop in a larger drop with reflections off either side of the drop.

2. EXPERIMENTAL

2.1 Surface Tension - Drop Period and Tensiopeak Period Relationship

A series of experimental and modelling results are presented here. The experimental studies were all done on a 9mm diameter drophead while the modeling work was done on an 8.5mm drophead. Unfortunately, it has not been possible to use the same diameter and designs for the two studies as the modeling work came after the experimental and is using the latest technology.

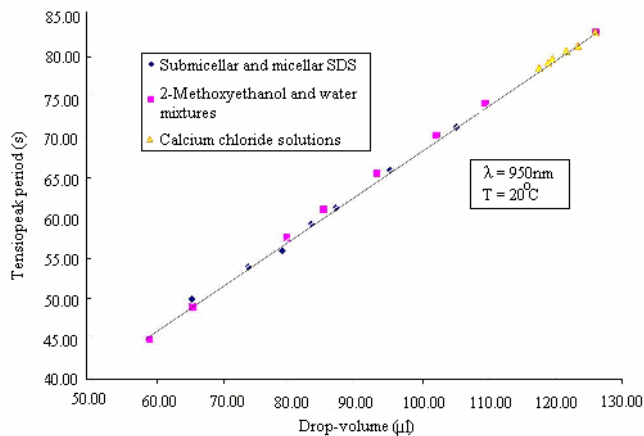


Figure 3: Tensiopeak period (t_3) variation with drop volume (V_D) for a number of typical solutions.

Figure 3 shows the experimental linear results for the relationship between tensiopeak period (t_3) and drop volume (V_D) for a range of non-surfactant liquids. Drop volume (V_D) is related to drop period (T_1) as follows:

$$V_D = qT_1 \quad [1]$$

Where V_D is in $\mu\text{l s}^{-1}$, the dosing rate q is in μl and T_1 in seconds.

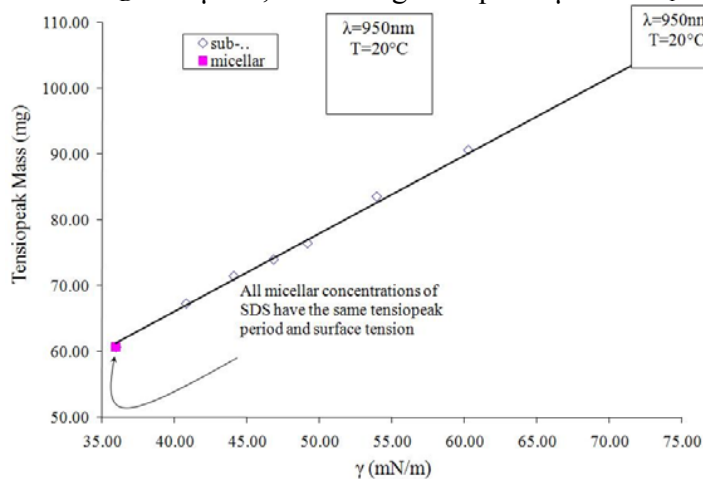


Figure 4. Tensiopeak mass against surface tension for a series of SDS solutions (both sub-micellar and micellar).

Therefore the tensiopeak period (t_3) is directly related to T_1 . It is possible to define a tensiopeak-period (t_3), tensiopeak-volume (V_3) or indeed a tensiopeak-mass (m_3) if the density (ρ) of the LUT is known, where t_3 and V_3 are the relevant time and volume at which the tensiopeak occurs. Tensiopeak mass (m_3) is equal to the product of t_3 and the flow rate- density product ($m_3 = \rho q t_3$). A typical dependence of tensiopeak mass on surface tension of a range of concentrations of sodium dodecyl sulphate may be seen in Figure 4. This relationship holds for both sub-micellar and micellar solutions

of these surfactant solutions. In a series of studies of several surfactants this important relationship holds¹¹. The relationship is linear with error bars that are too small to show on Figure 4 for both the micellar and sub-micellar concentrations of SDS. The graph slope is found to be 1.19 ± 0.02 . A linear plot with the same slope was also obtained for Triton X-100 and benzalkonium chloride.

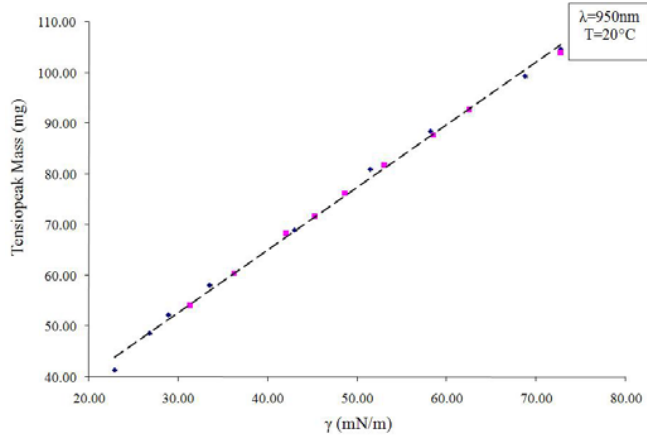


Figure 5. Variation in tensiopeak mass (m_3) with surface tension measurements of mixtures of (i) ethanol and water (ii) 2-methoxyethanol and water.

A typical dependence of tensiopeak mass on surface tension for a range of concentrations (0 – 100% (v/v)) of (a) ethanol / water and (b) 2-methoxyethanol / water is presented in Figure 5. There is an observed linear variation in tensiopeak mass with surface tension of mixtures of ethanol and water, with a slope of 1.20 ± 0.020 . The same results have been found for mixtures of (i) ethanol and water and (ii) 2-methoxyethanol and water.

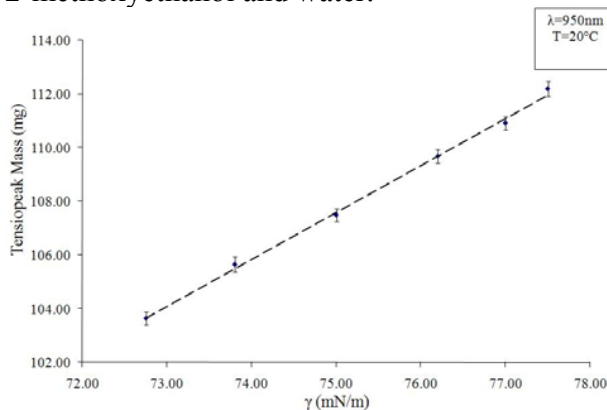


Figure 6. Variation in tensiopeak mass with tensiographic surface tension of a range of concentrations of calcium chloride.

There is a negligible difference in the slope of tensiopeak mass versus surface tension for both series of alcohols in water as confirmed from the error in slope. Significantly, this is the same slope that is observed for surfactant solutions. Figure 6 shows the variation in tensiopeak mass with surface tension for a range of salt solutions. It is important to note that these results are showing an experimentally different slope to that obtained for alcohol, surfactant and other solutions.

2.2 Modeling of drop period and tensiopeak period

The modeling of the tensiotrace has been described elsewhere¹² but is accurate qualitatively and quantitatively. A study of the tensiopeak mass on surface tension of

calcium chloride has been made and it is found that all salts analysed sit on the same first-order dependence. There is an observed linear empirical variation in tensiopeak mass with surface tension of a range of concentrations of CaCl_2 with a slope of 1.75 ± 0.020 . This dependence has a significantly higher slope than obtained for water, surfactants and mixtures of alcohol and water. The modeling of this result is perhaps best done in a slightly different way to the above. We can see that there is a relationship between drop period and tensiopeak period and mass.

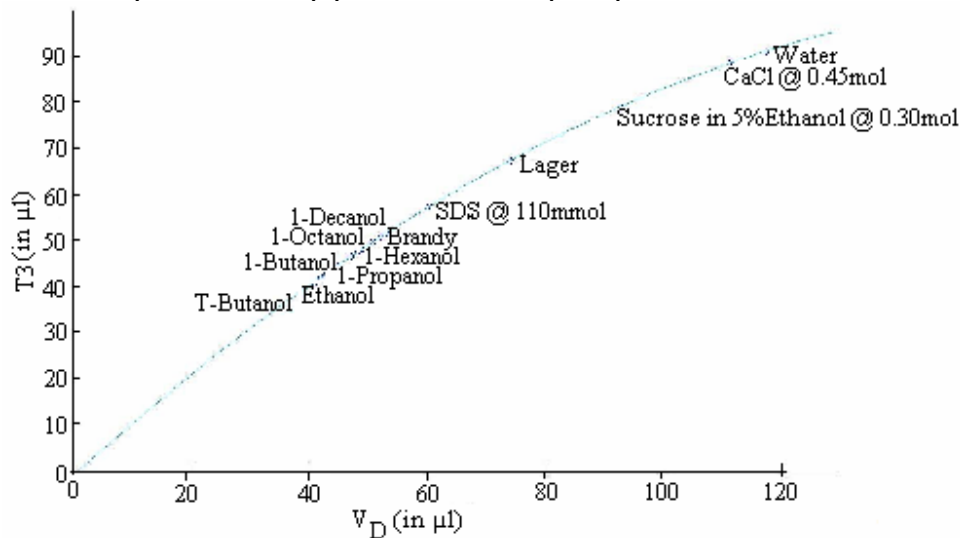


Figure 7. Modeling results for a wide range of liquids for t_3 and V_D results.

This modelling study confirms that for an 8.5mm quartz drophead that t_3 and V_D are related by a second order relationship. This differs slightly in form to the linear relationship found in the experimental study but clearly doing this study in two parts and finding two linear relationships strongly suggests that in fact a second-order relationship exists. Theoretically the modeling study is reporting unequivocally a single second-order relationship¹³. The surface tension can thus be determined from the tensiopeak period via standard tensiometric methods and this means that there is no need for the drop to detach from the head in order to make this measurement. Dynamic studies of processes such as enzyme reactions can thus be carried out on a single drop quantum using pump control. The measurement procedure is to drive the drop volume past the tensiopeak volume in order to determine a surface tension, then to reduce the drop volume to below this instantaneous t_3 -volume and importantly before the drop separates, and then to continually repeat this measurement of surface tension. Computer control should allow new measurements of surface properties every few seconds using this technique and thus offer a new method of dynamic surface tension measurement on a single drop. This discovery should be a very useful and eminently practical method for surface science.

3. Conclusions

The experimental discovery of the drop period relationship with tensiopeak period is well established by an empirical study that has been repeated on three occasions. The modeling results confirm the findings¹⁴. The question arises as to if there is a theoretical reason for this relationship. The best guess at this point is that the careful engineering of the drophead has produced a tensiotrace that for all liquids generates a tensiotrace close to the end of the drop cycle. Given the proximity of the tensiopeak to the drop separation for all liquid types, perhaps this is just a contrived relationship in

which there are no underlying physical reasons connecting the two phenomena. An investigation needs to be conducted to determine if there is a theoretical connection between T_1 and t_3 .

Secondly two experimental relationships for liquids were found with a unique linear dependence for salts, while other liquid types all fall on a single linear relationship. The modeling study has shown that there is one second order relationship for all liquids. While the modeling work strongly supports the experimental findings unfortunately this does not provide any analytical connection, but merely produces theoretical graphs confirming the relationship. This discovery however does mean in practice that with programmed volume control the repeated measurement of surface tension is possible on a single drop that is sitting on a drop head. The instrument would find many practical advantages in studies of surfactants, proteins-enzymes, biomolecules and mixtures of these molecules. The repeated oscillation in drop volume to keep tracking any changes in the surface property from changes in t_3 would be a practical limitation of the method if formation of complex structures on the drop surface could occur. The profile analysis tensiometer (PAT) can currently only track changes in equilibrium drop shapes for which Laplacian profiles apply and here a real potential advantage of the tensiographic method is beginning to emerge for surface analysis over the PAT method as the surface measurements do not assume equilibrium drop shape. The tensiographic method of course already offers a very significant supplementary quality bulk liquid characterisation of the LUT, which cannot of course be obtained by the PAT method. The discovery of this relationship is one that is perhaps of some real future importance.

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⁴ Rayleigh *Phil Mag.* **48** (1899) 321

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⁸ op.cit., Note 3.

⁹ K. Tiernan, D. Kennedy and N.D. McMillan, Tensiography instrument for measuring liquid material properties, *Materials and Design* **26** (2005) 197-201

¹⁰ N.D. McMillan, S. Smith and M. Baker, Tensiographic Drophead, 24 August 2006 WO 2006/087390 A1

¹¹ D. Morrin, Experimental Studies in Tensiography, Carlow, PhD (2007)

¹² op.cit Note 3 and P. Pringuet, Modeling Studies of Tensiography, PhD (Carlow 2009)

¹³ P. Pringuet, Modeling studies in tensiography, Carlow, PhD (2009)

¹⁴ Ibid.