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Commencement measurements giving fundamental surface tension determinations in tensiometry.

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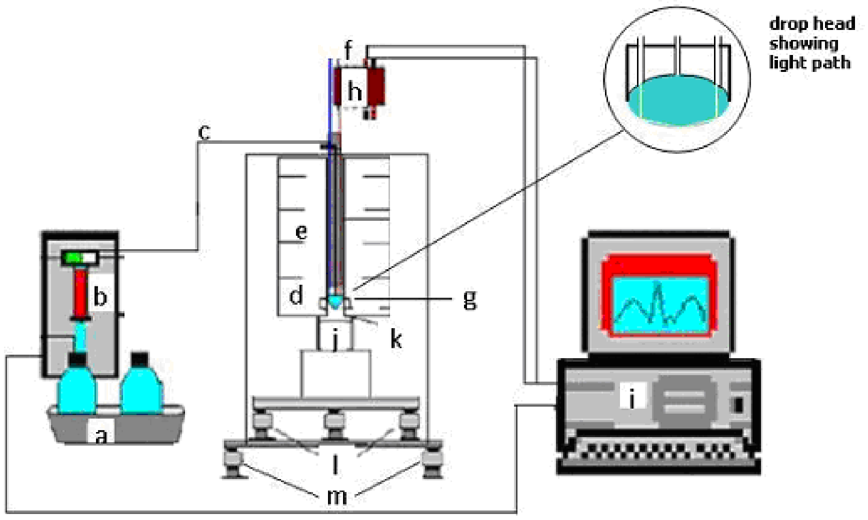
Abstract: This study provides experimental testing of a ray-tracing model of the tensiotrace that explores the measurement potential of a well-defined optical position in the tensiotrace signal known as the ‘commencement’. This point is defined as the first measureable optical coupling in the fiber drophead between source and collector fibers for light injected inside a growing drop. Tensiotrace ray-tracing model is briefly introduced. Empirical relationships of commencement measures from a wide-ranging study are presented. A number of conclusions can be drawn from the successful linking of computer predictions to these experimental relationships.

1. Introduction

1.1 Experimental

The instrument arrangement is shown in Figure 1



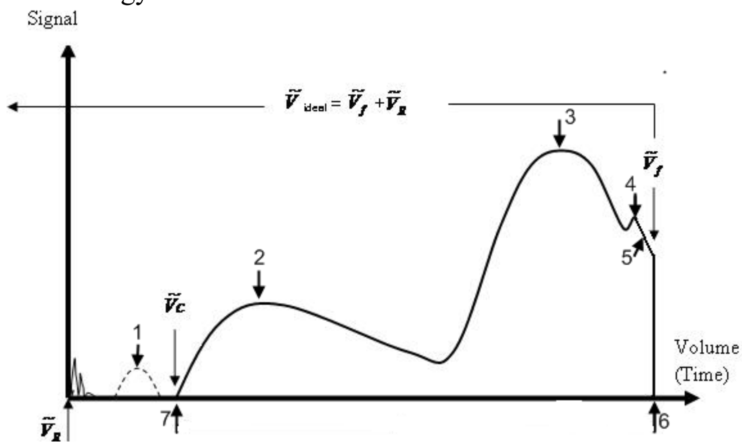
a	Samples for analysis	**h**	Detector
b	Stepper-motor-pump	**i**	Computer
c	Delivery tube	**j**	Chamber to ensure saturation of atmosphere
d	Drophead	**k**	Temperature sensors
e	Temperature control	**l**	Auto-levelling drives
f	Light source	**m**	Anti-vibration balancing feet
g	Optical eyes		

Figure 1 Schematic diagram of the tensiograph instrument.

The liquid **a**, which is to be analysed is pumped via the liquid delivery tube **c** to the drophead **d** using a motor stepper pump **b** and a pendant drop grows at a uniform volume rate (isochoric) in size until it separates from the drophead. Throughout this process, in what is in essence a single wavelength operation, light from a light emitting diode (LED) **f** is injected into the drop through the source-fibre and the reflected signal, picked up by the collector-fibre is transmitted to a photodiode **h**. The amplification of the low photocurrent into an adequate voltage signal is necessary before the signal is passed to an acquisition board [an electronic system based on a programmable interface controller (PIC) and other suitable electronics hardware] incorporated in a personal computer (PC) **i**. The optical eyes **g** sense the drop on the drophead – the initial trigger occurs when the initiation drop falls through the optical eye and triggers the start of the data acquisition.
This indicates when the measurement drop has arrived on the drophead and then the data acquisition continues until this drop falls off the drophead and the second trigger locates precisely the ending of recording of the tensiotrace (a data set recorded over the life cycle of the drop). Two-stage anti-vibration mounts **l** and **m** protect the drop from vibrations. The analogue to digital converter (ADC) of the acquisition board converts the analogue voltage (amplified optoelectronic signal from the detector) into a digital signal, which is then subsequently transferred to the memory of the PC where it is stored for later analysis. The source-detector employs a CCD (charged couple device) or CMOS (complementary metal oxide semi-conductor) detector in conjunction with a spectral source such as fibre deuterium, xenon, halogen or tungsten sources. Such a system provides a spectral array of tensiotraces, one for every measurement wavelength.

1.2 The Tensiotrace

The key concept of the tensiograph is that all the various physical and chemical processes that modulate the coupled light in the drop produce a signal, which is unique in a theoretical sense for every specific combination of properties of the liquid under test (LUT). These processes include partial reflection of the light beam inside the pendant drop, absorption of the light from chromophores in the liquid, scattering of the light from turbid particulate matter and changes in the emission angle from the source fibre. The detected light intensity is amplitude modulated during the life cycle of a drop i.e. the reflecting surface of the inner drop changes continuously. A tensiotrace (Figure 2) is a typical sensogram which is a very recent terminology.



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

The first-order peak is only observed in very special drophead designs. It is not seen in the current drophead design shown schematically in Figure 1 - the first order coupling is geometrically not possible because the measurement drop is too flat with the widely spaced fibres. The x-axis can be either volume or time as both are equivalent for constant volume delivery from stepper pumps. Two important measurands are noted: tensiopeak period or time to tensiopeak (t_3) and time of drop period (T_1).

The positioning of the fibres in the drophead has been engineered to optimise the measurement of various physical/chemical properties. The rainbow peak height and position in the tensiotrace is a good measure of refractive index. It gets its name from the fact that in rainbows a measurement of the angle of the bow to that of the observer provides a measurement of the refractive index of the liquid. The height of the tensiopeak provides a good measurand for determining the colour and/or turbidity of the solution in that the peak decreases respectively with the increasing absorptive or scattering power of the liquids. The drop period can be used to give a good measure of the surface tension/density ratio. Other physical measurements have been shown to be possible with the tensiograph, but despite the obvious usefulness of an instrument that provides so many measurements, the principal use of the tensiograph is as a fingerprinting technique. It has been demonstrated, over a considerable period of time that the combination of the complex of physical and chemical properties of the drop ultimately defines the form of the tensiotrace and thus the tensiotrace provides a very sensitive fingerprint technique for liquids, or indeed solid samples dissolved in a solvent.

1.3 The Ray-tracing Model of the Tensiotrace

The computer model is used to investigate theoretical issues regarding the tensiotrace. This RAST ray-tracing model is described in these proceedings by Pringuet et al[1]. We know that there are only numerical solutions to the Laplace-Young equation and it follows that there can only be numerical (computer model) solutions to the analysis of a tensiotrace. The drop shapes in our model are only dependent on the shape factor parameter $\beta_S = \frac{\rho g r_0^2}{2\gamma}$ where ρ is the density of the liquid, γ is the surface tension and r_0 is the drophead radius. It is clear that the tensiotrace is also sensitive to both the refractive index and absorbance (turbidity is not considered here but is a dimensionless quantity that is defined in an analogous way to absorbance). The model takes into account all the physical properties of the drop-under-test (DUT) and is an excellent qualitative tool, but in addition can deliver quantitative relationships such as those below in which the empirical relationships are quantitatively predicted. It will not be necessary to elucidate this RAST model further here.

2 Commencement Measurement

The only existing tensiograph study of remnant drop relationships are those by Gao and Zeng[2].They used the vibration of the remnant drop to investigate the size of this drop. The drop volume is $\overline{V_R}$ in Figure 2.This was a method suggested initially by McMillan, Feeney et al[3] and developed then by McMillan, Carbery et al[4]. The real issue of studying the size of the remnant drop has not been advanced much in these studies that were somewhat limited and largely qualitative. The new work reported here is very different and shows for the first time the real power of tensiography in dealing with these vital issues of defining the volume of a remnant drop and thus experimentally advancing the work of Harkins and Brown[5] and supplementing the recent theoretical contribution by Basaran[6]. The rainbow peak commencement is a very precisely defined point of optical coupling when a measurable amount of light reaches the detector. Figure 3 shows drawings taken from camera recordings of remnant drops of various liquids.

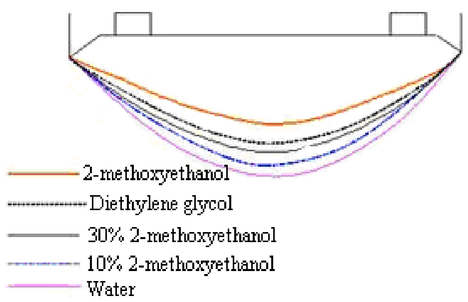


Figure 3. Drawings made from camera images of various remnant drops showing physically the variability in these drops for different liquids

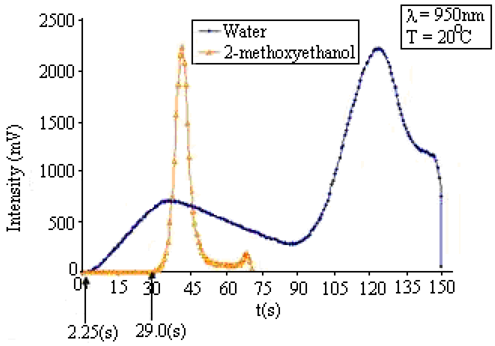


Figure 4. Tensiotraces of water and 2-methoxyethanol showing large variation in the measured commencement position

These experimental studies on the remnant drop underlie all the subsequent discussion in this section as tensiography provides a measurement tool for studying the remnant drop.
Figure 4 shows the experimental results for the very striking variability in the measured rainbow peak commencement for a water and alcohol type drop, illustrated by a typical representative of this liquid type 2-methoxyethanol. The measured times are for water 2250ms and for ethanol 29000ms. These two liquid types are commonly taken as the two extreme liquid types.
It has been shown that it is not possible to accurately determine the rainbow peak commencement of these traces by eye as replicate measurements show too big a standard deviation. However, an accurate method has been used to determine the 'commencement point' of the tensiotrace using specially written software. In brief, the software smoothes the data as can be seen in Figure 5 and then with a set threshold value determines a commencement point as so defined by the threshold. The practical results show that this measurement is both precise and accurate and provides an excellent measurement point.

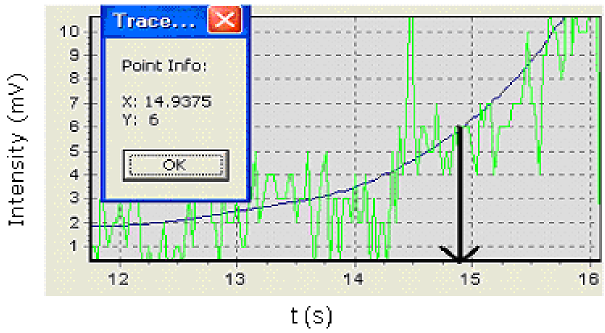


Figure 5. Enhanced trace of a typical tensiotrace using Trace-miner software for the determination of the rainbow peak commencement.

3.Comparison of Experimental and Theoretical/Modeling Results

3.1 Remnant Drop and Rainbow-peak Commencement Studies

Figure 6 shows the modelling results of the series of alcohols for remnant drop volume against the shape factor (β_S). It is clear that the modelling predicts a very linear relationship, which of course underscores the fact that correction factors have well defined mathematical relationships with this shape factor. The RAST model predicts this variation.

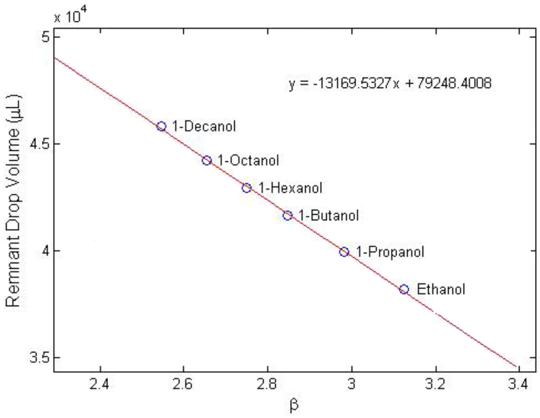


Figure 6 Analysis of remnant drop volume against the shape factor (β_S) on a 8.5mm drophead for a series of alcohols.

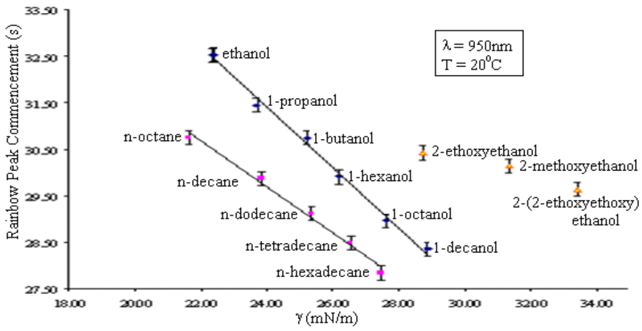


Figure 7. Relationship between rainbow peak commencement and surface tension values for alkane and alcohols.

The graphical plots of a series of rainbow peak experimental results on commencements measured against surface tension (γ) for a series of alkanes and alcohols are shown in Figure 7. It shows that the family of chemicals lie on two different lines. For the branched alcohols no trend line is shown but the four chemicals 1-butanol, 2-ethoxyethanol, 2-methoxyethanol and 2-(2-ethoxyethoxy) ethanol; lie on a second order trend line. The RAST model predicts this variation.

It is found that R_{RP} divided by refractive index (water being used as a standard here) against normalised surface tension or β_S is a first-order relationship. R_{RP} is defined as the ratio of rainbow peak commencement to rainbow peak commencement of water The experimental and modelling results for R_{RP} against normalised surface tension (or β_S) is a straight line for all Micellar surfactants although the ageing of the surface is an issue here and sufficient time must be left in order to bring the surface to an equilibrium situation. A universal relationship appears to exist for all liquids for R_{TP} (Ratio of the tensiopeak period using water as the reference liquid) against normalised drop volume. This is a significant experimental finding for this study[7].

Drop volume of course, because of its historical importance in the classical surface science technique of tensiometry, can be considered as the primary measurand of tensiography. Several other results that show first-order tensiographic relationships exist and Morrin[8] has documented many more empirical experimental findings and indeed even more low order trend-lines.

The results of a recent experimental study show that the "tensiopeak-period" (time to reach tensiopeak) (t_3) accurately predicts the value of the drop period T_1.

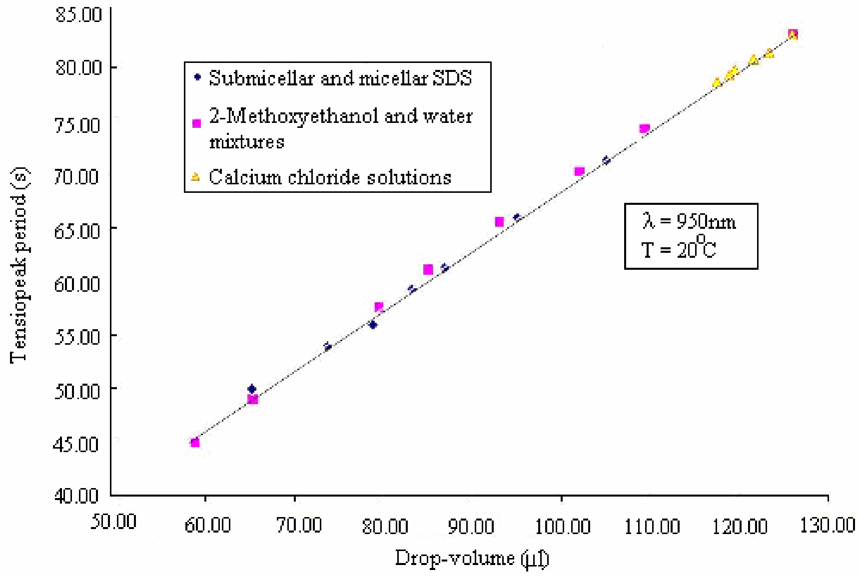


Figure 8. Tensiopeak period variation with drop volume.

Figure 8 shows the experimental linear results for the relationship between tensiopeak period (t3) and drop volume ($\widetilde{V}_f$) for a range of non-surfactant liquids. Drop volume is related to drop period (T_1) as follows:

$$\widetilde{V}_f = qT_1$$

where q is the liquid flow rate.

The significant advantage of using t_3 is that the drop does not separate from the drophead. Further results confirm the relationship between T_1 and t_3 for a wide range of liquids. These experimental studies were all done on a 9mm diameter drophead. Modelling work confirms these results. This relationship has been investigated by McMillan et al[9]. The limitation for the tensiometric method that depends on correction factors is highlighted from the chaotic and obviously unpredictable process revealed in Carbery's camera studies[10]. These chaotic processes mean in practice tensiometric correction factors will not be defined with accuracy.

4. Conclusion

Commencement is extremely well defined point in this optical signal and a reliable experimental method has been devised to obtain a quantitative measure of this point. The study reveals that commencement is a very useful tensiographic measurand. The commencement measures in extensive studies of families of chemicals, surfactants, salts and other liquids have been shown to graphically deliver useful surface measurements.

The tensiotrace is of course an optical signal derived from the evolving dropshape of a pendant drop. It is well-known that pendant dropshapes are universal set of curves that can be represented in a dimensionless form predicted by the dimensionless β_S factor. The tensiotrace is obtained from the RAST ray-tracing model but this trace is generated not only from dropshapes but also refractive index, absorbance and turbidity which are all dimensionless quantities. Some experimental results have been presented demonstrating that tensiographic measurements can directly predict surface tension of the liquid-under-test (LUT). Taken in the whole, these fact suggest that tensiography like profile analysis tensiography (PAT) provides measurements of the LUT or DUT that are based on similar dimensionless methods. This conclusion regarding tensiography is of some real importance as the PAT method is becoming accepted as one of the fundamental method in surface science precisely because of these measurement considerations.

6. References

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