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Effects of injection angle on the measurement of surface tension coefficient by drop weight method

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The drop weight method for surface tension measurement is based on the weight of drops detached from a nozzle. The original idea was based on a postulate introduced by Tate (On the Magnitude of a Drop of Liquid Formed Under Different Circumstances, *Philos. Mag.* 27, 176–180, 1864), assuming that the weights of an ideal pendant drop and a detached ideal drop are identical, and that this weight is equal to the surface force that holds a drop attached to the nozzle. To consider the real volume of a drop that detaches from a nozzle, the method required a correction factor. Harkins and Brown suggested such correction factors for vertical injection from a nozzle. In this study, a correction factor for injection at different angles is presented and some of the hydrodynamic effects on surface tension measurement based on the drop weight method are studied. In addition, a model is introduced for the detachment time of drops in directions other than the vertical direction

Keywords: fluid property measurement; surface tension; drop weight method, drop formation; inclined pendant drops

1. Introduction

When a liquid ejects at an infinitesimal flow rate from a circular, horizontally-cut, sharp-edged tip of a nozzle into a quiescent, immiscible fluid medium, a quasi-static growth of a pendant drop is observed. The theoretical basis of the drop volume method was founded at the beginning of this century by Lohstein [1]. The mass (or volume) of drops detaching from nozzles in a quasi-equilibrium condition is proportional to interfacial forces in the fluid; this was first suggested by Tate [2]. His law, later modified by Harkins and Brown [3], stated that the surface tension force of a liquid is equal to the weight of a detached drop. Tate's law, in its initial form, ignored the fact that as a drop is detached a portion of the pendant drop remains attached to the nozzle; this hypothesis resulted in overestimating surface tension coefficients. Considering the overestimation, Harkins and Brown [3] introduced a correction factor, F . This factor decreases surface tension values on the ground that, firstly, after a drop is released, a portion of the liquid (depending on the diameter of nozzle and the volume of a detached drop) does not leave the nozzle

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(see Equation (1)). Secondly, the boundary tension forces are not practically vertical. Third, there is a pressure difference across the curved interface. Accordingly, the shape of pendant drops is another crucial parameter in the surface tension measurement by the drop weight method.

$$\sigma = \frac{Fmg}{r}, \quad (1)$$

where σ , m , g and r are the surface tension coefficient, drop mass, gravity, and radius of the tip of nozzle, respectively; F is the correction factor tabulated by Harkins and Brown. Later, the tabulated correction factors were fitted on a quadratic equation based on a regression analysis [4]. Campbell [5] used the drop weight method with slight changes; he eliminated the unknown coefficient (i.e. the correction factor) in the relation for calculating surface tension by comparing results for the fluid under study with a fluid with known surface tension. His method required the surface tension of a reference fluid and its density difference with respect to the surrounding fluid. This density difference was required to be very close to the density difference between the measured fluid and its surrounding medium. Although he claimed that this method was less sensitive to errors in the density of fluids, the original form of the drop weight method (with the Harkins and Brown correction factors) was being used in most of the studies on the drop weight method, such as a study by Tornberg [6]. Mori [7] critically reviewed the literature on different suggestions for the correction factors. According to his survey, the correlation introduced by Heertjes *et al.* [8], Equation (2), applicable for the range $0 \leq \psi = (r/V^{1/3}) \leq 0.3$, was the most accurate suggestion for the correction factor (V is the volume of pendant drops before detachment).

$$F = \frac{1}{\pi^2} [0.14782 + 0.27896\psi - 0.166\psi^2]. \quad (2)$$

Compromising accuracy and the ease of use for predicting the correction factor with the value $\psi \leq 0.7$, Mori introduced a correlation,

$$F = \frac{1}{2\pi} \left[0.6 + 0.4 \left(1 - \frac{D}{1.4} \left(\frac{1}{2\pi FV} \right)^{1/3} \right)^{2.2} \right]^{-1}, \quad (3)$$

where D is the diameter of the nozzle and V is the volume of the pendant drop at any instant of time. A detailed error analysis of the drop weight method for surface tension measurement was presented by Earnshaw *et al.* [9]. According to their analysis of drop weight method, the influence of an unknown correction function was introduced in the square bracket in Equation (4).

$$\left(\frac{\varepsilon\sigma}{\sigma} \right)^2 = \left(\frac{\varepsilon\Delta\rho}{\Delta\rho} \right)^2 + \left(\frac{\varepsilon r}{r} \right)^2 \left[1 + \Psi \frac{\Phi'}{\Phi} \right]^2 + \left(\frac{\varepsilon V}{V} \right)^2 \left[1 + \frac{\Psi}{3} \frac{\Phi'}{\Phi} \right]^2, \quad (4)$$

where ε represents experimental uncertainties on observable parameters; $\Phi = 1/2\pi F$, and Φ' is the partial derivative of Φ with respect to r . A good historical survey of drop volume tensiometry is given in [10].

The drop weight method was also applied for measuring the dynamic surface tension coefficient. Kloubek [11] recommended that the drop weight method enable

(with the help of empirical corrections) to determine the dependency of the dynamic surface tension on the static surface tension within a range from several seconds to an equilibrium value. He demonstrated that the tips of common capillaries implemented in tensiometry often do not meet conditions enabling the application of the Harkins and Brown factors. He also showed that the factors are not suitable for dynamic surface tension measurements. The minimum surface age of drop weight technique was extended by Henderson and Micale [12] to 20 ms; they also observed a linear relationship between the drop mass and the surface tension coefficient at constant flow rate, viscosity and tip radius. Based on their results, the drop mass was increased as the flow increased up to a certain limit, then an increase in the flow rate decreased the drop mass. In a comprehensive study, Miller *et al.* [11] investigated the hydrodynamic effects on measurements with the drop volume technique at small drop times. They reported that the drop weight method can be applied to short drop times when the so-called hydrodynamic effects are taken into account. Ignoring these effects leads to higher surface tension values. According to their study, the liquid's viscosity also affects the hydrodynamic effects and leads to even higher surface tensions with the increase of viscosity and radius of nozzles.

The drop weight method was also applied in surface tension measurements at temperatures higher than the room temperature and to liquids other than water-like liquids. It is possible to measure surface tension coefficients of molten drops produced by heating the tip of different wires. Such measurements were performed by Calverley [13] (tungsten), Peterson *et al.* [14] (titanium, zirconium and hafnium), Tille and Kelly [15] (titanium) and Desforges and Charles [16] (iron). Moreover, Vinet *et al.* [17] applied the method to some refractory materials and developed the Harkins and Brown correction factor in its untabulated range. They discussed the validity of their study via a dimensional analysis, which showed that the correction factor, F , depended on two dimensionless parameters. In another study, they demonstrated that the correction factor can be derived from a momentum balance written just before the release of a drop. Equation (5) shows a general correlation for the correction factor in terms of radius and height of the neck, r_0 , z_0 (Figure 1), radius of nozzle, r , curvature at the apex, b , density difference, ρ and surface tension coefficient, σ , of the fluid [18].

$$F = \frac{r_0}{r} \left[1 - \frac{r_0}{2} \left(\frac{2}{b} - \frac{\rho g}{\sigma} z_0 \right) \right]. \quad (5)$$

Since this relation depends on parameters that are practically unknown, such as radius of the neck, height of the neck and curvature at the apex, it cannot be used to find a value for correction factor; however, it is the first theoretical justification for the correction factor. Vinet *et al.* [19] applied the drop weight method to some industrial alloys. They insisted on the simplicity of the drop weight method, although it cannot be used for temperature coefficient measurement of the surface tension. In a detailed study on the drop weight method, Yildirim *et al.* [20] tried to put the currently empirical drop weight method on a firmer foundation by analysing the dynamics of drop formation by means of one-dimensional slender-jet equations. From a dimensional analysis, they discussed that there must exist a functional relationship between the dimensionless radius ($\psi = \frac{r}{\sqrt{r_0}}$), Bond number ($Bo = \frac{\rho g L^2}{\sigma}$), Ohnesorge number ($Oh = \frac{\mu}{\sqrt{\rho \sigma L}}$) and Weber number ($We = \frac{\rho v^2 L}{\sigma}$). Based on their

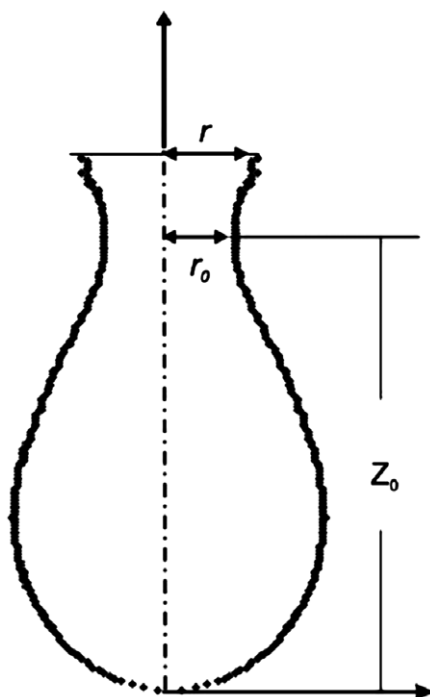


Figure 1. Geometry of a pendant drop at the instant of detachment. At quasi-equilibrium state, detachment happens only because of gravitational force.

analysis and computations, they deduced that when $We \rightarrow 0$ the dimensionless radius depends solely on the Bond number; this is shown in Equation (6):

$$Bo = 3.60\psi^{2.81}. \quad (6)$$

Recently, Lee *et al.* [21] investigated the validity of correction factors for the drop weight method at different ranges of $r/V^{1/3}$. They concluded that more investigations would be required to form a rigid theory for the drop weight method. Most of the results available in the literature on the surface tension coefficient of metals or alloys at liquid state are based on the drop weight or the pendant drop methods. It is noteworthy that the majority of these studies was based on the correction factors suggested by Harkins and Brown, originally derived for liquids with low surface tension (e.g. water). The factors were tabulated for room temperature, in the absence of any possible oxidation. In addition, with no exception, all studies have considered the vertical injection of fluid from a nozzle or capillary tube. The vertical configuration is also the case for all measurements conducted at higher temperatures (melting vertical metallic samples).

The objective of this study was to investigate the effects of the angle of nozzles on the correction factors for surface tension measurement. The results for this study contributed to the accuracy of a new surface tension measurement method at high temperatures in which horizontally aligned rod-shaped samples of high melting point

materials were heated and the drop formation due to melting was mimicked by horizontal drop injection [22,23].

2. Experimental method

A simple experimental setup was used to inject distilled and de-ionised water at different angles. Water was ejected through different nozzles by a pump (SAGE Instruments Inc., Freedom, CA, USA 34-1B) capable of adjusting flow rates to 0.23, 0.34, 0.78, 1.6, 2.2, 3.3, 5.5, 8.8 and 13.2 ml h⁻¹. Nozzles were stainless steel, regular bevel, 18G 1½, 19G 1½, 20G 1½ (Precision Guide). Tip of the nozzles, with the outer diameters of 1.24, 1.08 and 0.89 mm, were cut at 10°, 45°, 60° and 90°. Figure 2 shows a set of nozzles arranged horizontally with different angles at the tip. The measurements were performed at room temperature. According to the literature [24], the static surface tension and density of water at this temperature are 0.0728 N m⁻¹ and 998 kg m⁻³, respectively. The drop formation and detachment processes were recorded with a high-speed charge-coupled device (CCD) (Photron Corporation Ltd, FastCam ultima 1024, San Diego, CA, USA). The images were used for surface tension measurements based on the Young–Laplace (YL) [25,26] pendant drop profiles [27]. To reduce possible errors in the measurement of drop mass and detachment time, results for each case were averaged over 10–15 experiments. Accuracy in the measurement of mass was ±0.001 g. The drop formation was

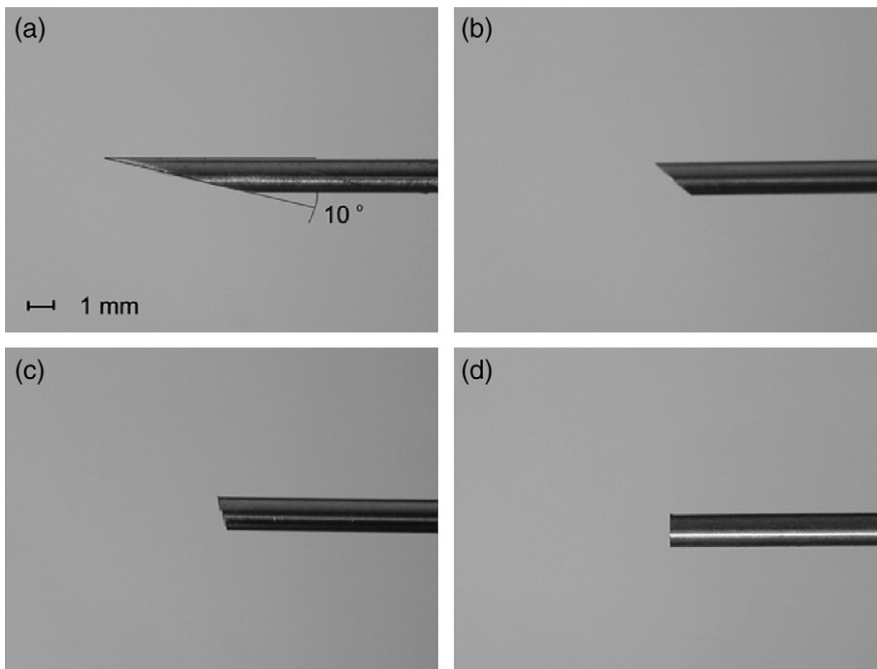


Figure 2. Stainless steel nozzles (outer diameter (OD): 1.24 mm, inner diameter (ID): 0.84 mm) used for injection in horizontal configuration with different angles of the tip: (a) 10°, (b) 45°, (c) 60° and (d) 90°.

recorded at the rate of 125 frames per second, and the accuracy in measuring detachment time was ± 0.01 s.

2.1. Pendant drop formation from horizontal nozzles

Liquids ejected from a nozzle in a quiescent immiscible medium are subject to three major forces: gravitational, inertial and surface tension forces. Accordingly, at low flow rates, the evolution of a pendant drop is due to the changes in the ratio of surface tension force and weight of the drop. Since the direction of gravity is always vertically downward, a change in the direction of injection (either a 90° tip-angle nozzle at different angles, or a horizontal nozzle with different tip-angles, (Figure 3) affects the internal flow such that the flow is not similar to the flow when the liquid is ejected from a vertical nozzle. Figure 3(a) illustrates drop formation from a 90° tip-angle nozzle at three different angles (vertical, inclined (45°) and horizontal). Moreover, Figure 3(b) shows horizontal injections from nozzles with the same diameter but with different tip-angles. The cases shown in this figure were at $t = 28$ s

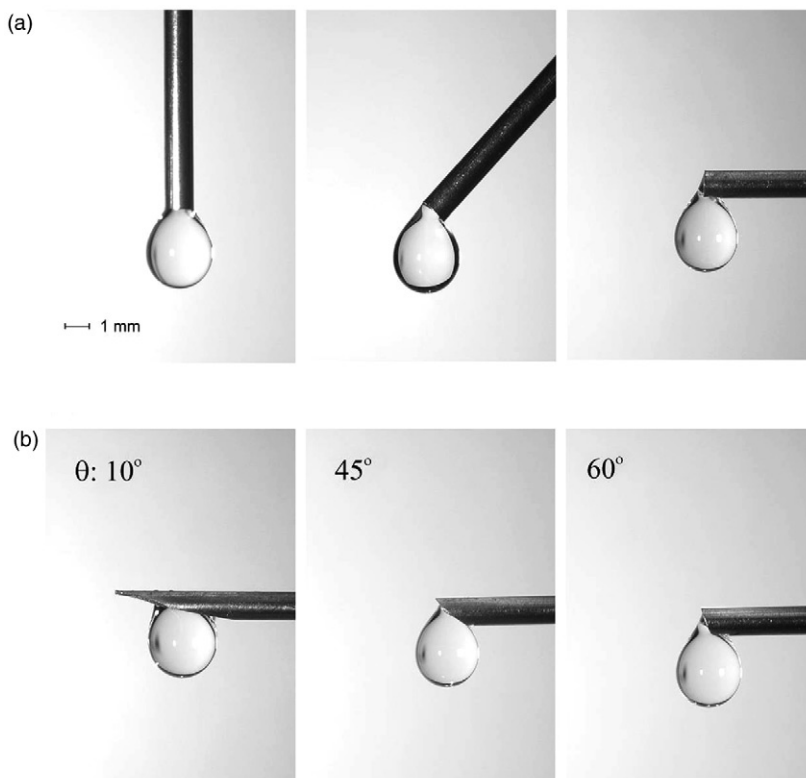


Figure 3. Drop injection from nozzles, OD: 1.24 mm, ID: 0.84 mm, in two different configurations with different tip-angles; flow rate: $0.44 \mu\text{s}^{-1}$; all frames at $t = 28$ s (a) angle of nozzles: 0° , 45° and 90° (b) horizontal injection for different tip-angles: 10° , 45° and 60° .

after the detachment of the previous drop for a nozzle with 1.24 mm diameter and a flow rate of $0.44 \mu\text{l s}^{-1}$.

2.2. Similarities in drop formation due to melting and liquid ejection from nozzles – horizontal configuration

In a method for measuring surface tension at high temperatures [23], we observed that melting a horizontal rod-shaped sample produces a pendant drop with an interface that forms an angle with respect to the rod. In order to study the nature and effects of such an angle, we investigated the drop formation due to the liquid ejection from nozzles at different angles.

In both scenarios – melting a rod and liquid ejection from a nozzle – gravity and surface tension are the dominant forces shaping the pendant drop (slow melting). Theoretically, contact angle between a liquid and solid of the same material is zero, whereas in the case of liquid injection, the liquid may wet a nozzle at different angles (depending on the liquid and the material of nozzle). Accordingly, melt wets its rod more than a drop which is hanging from a nozzle. Other than a region in the vicinity of the interface between solid, liquid and gas phase, the general behaviour of drop formation and detachment are similar in melting a rod and dripping from a nozzle. For instance, Figure 4 shows the melting of paraffin and copper rods. The paraffin and copper rods have diameters of 5.4 and 5.0 mm, respectively. These rods were heated from one side, with a flame (for paraffin) and a radio-frequency inductively coupled plasma (rf-ICP) torch (for copper). As is shown in this figure, drops attached to the rod wetted the rod completely; whereas in drop formation from a nozzle, the contact angle is larger, e.g. the drop does not seem to wet the nozzle.

In melting, the three-phase-line formed at almost a fixed angle, which depended on the diameter of rod. According to this figure, the angle of interface between liquid and solid paraffin, or liquid and solid copper, was about 40° . For a copper rod with a diameter of 1.16 mm this angle was repeatedly measured as 19° .

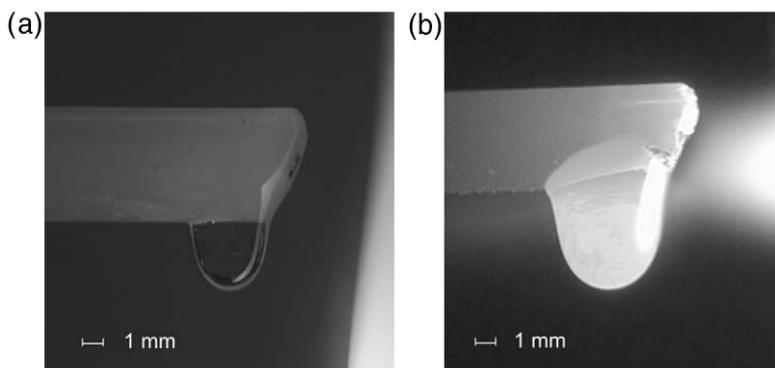


Figure 4. Drop formation due to the of heating of the tip of rods (a) paraffin; diameter: 5.4 mm; melting point: 67°C (b) copper rod 99.999%; diameter: 5.0 mm; melting point: 1058°C .

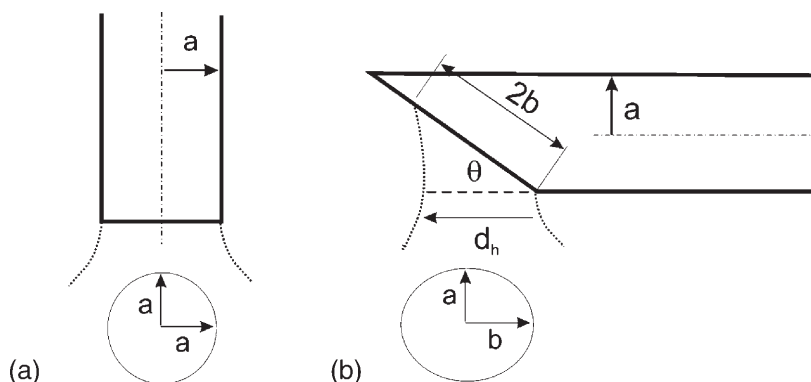


Figure 5. Difference in the perimeter of the interfacial line between the liquid and the nozzle in vertical and horizontal configuration with different tip-angles.

2.3. Geometrical consideration in interfacial force balance for liquid ejection at different angles

Figure 5 compares the length of three-phase-line in two different configurations: vertical injection with 90° tip-angle and horizontal injection with a tip-angle of θ° . Based on this figure, the ratio of the interfacial lengths, l , in vertical to horizontal nozzle is as follows:

$$\frac{l_V}{l_H} = \frac{a}{\sqrt{\frac{1}{2}\left(a^2 + \frac{d_h}{4\cos^2\theta}\right)}}, \quad (7)$$

where a and θ are the radius of nozzle and the tip-angle, respectively; d_h is shown in Figure 5. For example, for a 45° tip-angle, before the instant that weight overcomes surface tension force, d_h is larger than $2a$ (the drop is growing; however, it has not started moving downward). This results in a difference of 20% in the interfacial length, e.g. up to $\sim 0.014 \text{ N m}^{-1}$ underestimation in surface tension measurements for water. In the next sections it is shown that a practical correction factor that can be used in the special case hypothesised above is not exactly 20% different from the Harkins and Brown correction factors.

Note that as the angle of injection is changed, the correction factors prescribed for the drop weight method are not only affected by the change in interfacial length, but also by the change in the fluid flow. However, this shows that the correction factors suggested by Harkins and Brown are not applicable for dripping in configurations other than the vertical injection. As noted before, validity of the correction factors for dynamic surface tension measurements by the drop weight method was questioned by some researchers [7,8].

3. Dynamic surface tension measurement based on the profile of pendant drops

In order to investigate the effects of the angle of drop ejection on surface tension coefficients measured by the drop weight method, pendant drop profile matching

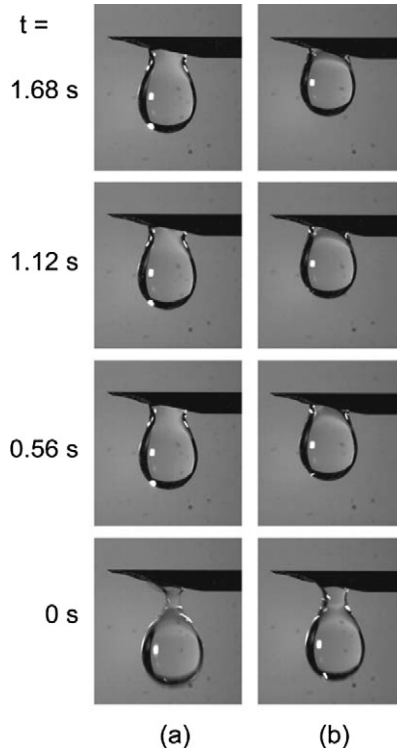


Figure 6. Drop formation of water at the tip of a horizontal nozzle (OD: 1.24 mm, ID: 0.84 mm) angle of the tip is 10° , at different flow rates: (a) $0.44 \mu\text{l s}^{-1}$ and (b) $3.67 \mu\text{l s}^{-1}$. The times shown are based on the last frame before the detachment; accuracy: 8 ms.

(YL profiles) [23] was used to measure the surface tension reference values. The drop shape technique was first implemented by Neumann and Spelt [25]. To measure the surface tension coefficient based on the YL profiles, images of drops were analysed with an image analysis algorithm [28]. Two series of high-speed images are shown in Figure 6. The images correspond to flow rates of 0.44 and $3.67 \mu\text{l s}^{-1}$. Flow rates in both cases were relatively low, as a result, profiles resulted from the experiment were in good agreement with the quasi-equilibrium profiles suggested by Young and Laplace (Figure 7). The YL formulation is described in Appendix A. Figure 7 shows the results of dynamic surface tension measurement by fitting theoretical profiles on the experimental profiles. The Reynolds number used in the figure was defined as $\text{Re} = \frac{\rho v d}{\mu}$, where d the diameter of nozzle. According to the figure, the quasi-equilibrium assumption was valid for the range of flow rates studied here. Note that the surface tension values measured by the profile fitting were higher than the surface tension values at lower flow rates. This effect was one of the hydrodynamic effects that Tornberg [6] and Miller *et al.* [10] described in their dynamic surface tension measurement methods by using the drop weight method for vertical dripping. Since the flow rate in set (b) of Figure 6 is 8.3 times higher than the flow rate in set (a), necking occurred in a much shorter period of time. Basically, when the flow rate increases, the weight of the drop increases faster; this results in quicker detachment of the drop from the nozzle.

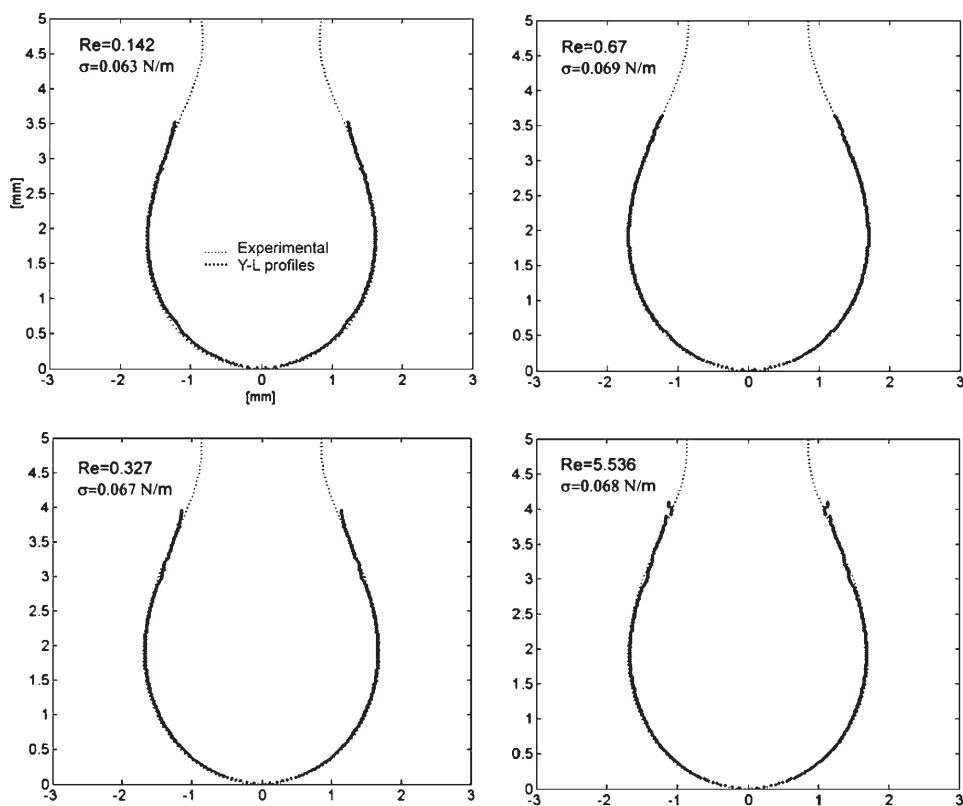


Figure 7. Fitting YL profiles on the experimental profiles of horizontal injection of water from a nozzle with tip-angle of 10° at different flow rates. Profiles illustrated for each case correspond to 20 ms before the detachment.

4. Results and discussion

Figure 8 shows the surface tension coefficients measured from horizontal nozzles with different tip-angles. According to this figure, for very small Reynolds numbers ($Re < 5 \times 10^{-4}$), as the Reynolds number is increased, the surface tension coefficient increases. However, as the Reynolds number is increased, the surface tension coefficient increases up to a maximum value. For small tip-angles, the interface between water and nozzles is larger; this can be the reason for the differences in the results. During the drop formation process, the higher the tip-angles, the more the direction of velocity vectors changes. This effect on the flow is more difficult to investigate experimentally. Theoretically, the 45° case is the optimum case in terms of less deviation in the flow direction. Each point in Figure 8 represents the average of results for 15 drops.

In a comparison between the drop formations from a 90° tip-angle at horizontal, inclined (45°), and vertical configurations (Figure 9), it was revealed that ejection at 45° is very similar to injection from a horizontal nozzle with 45° tip-angle. Since the Harkins and Brown factors were developed for vertical configuration, dynamic surface tension coefficients for the vertical case were in agreement with the literature

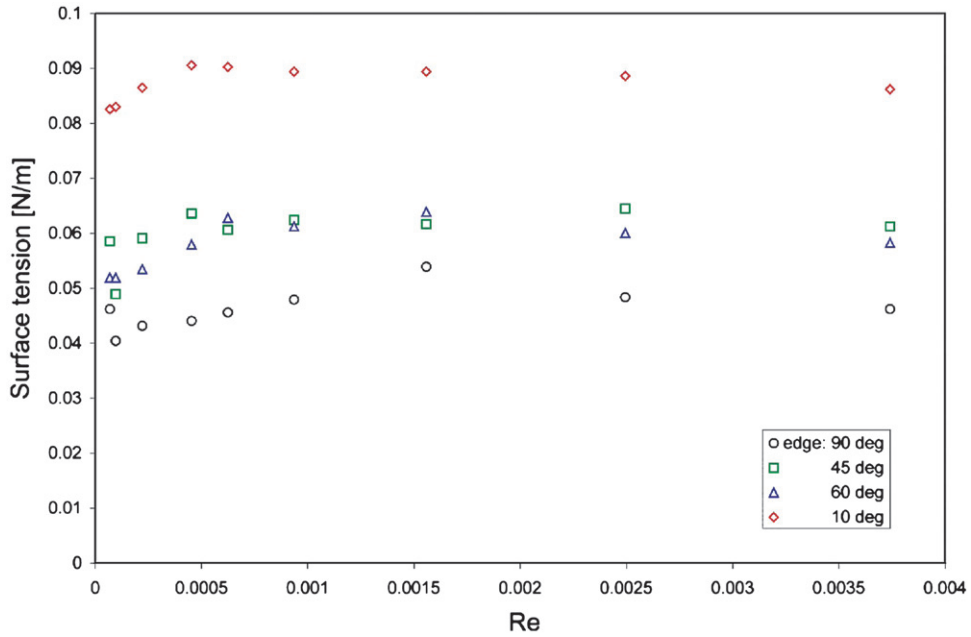


Figure 8. Surface tension, measured with the drop weight method and Harkins and Brown correction factors at different flow rates for horizontal injection with different tip-angles; nozzle OD: 1.24 mm (water).

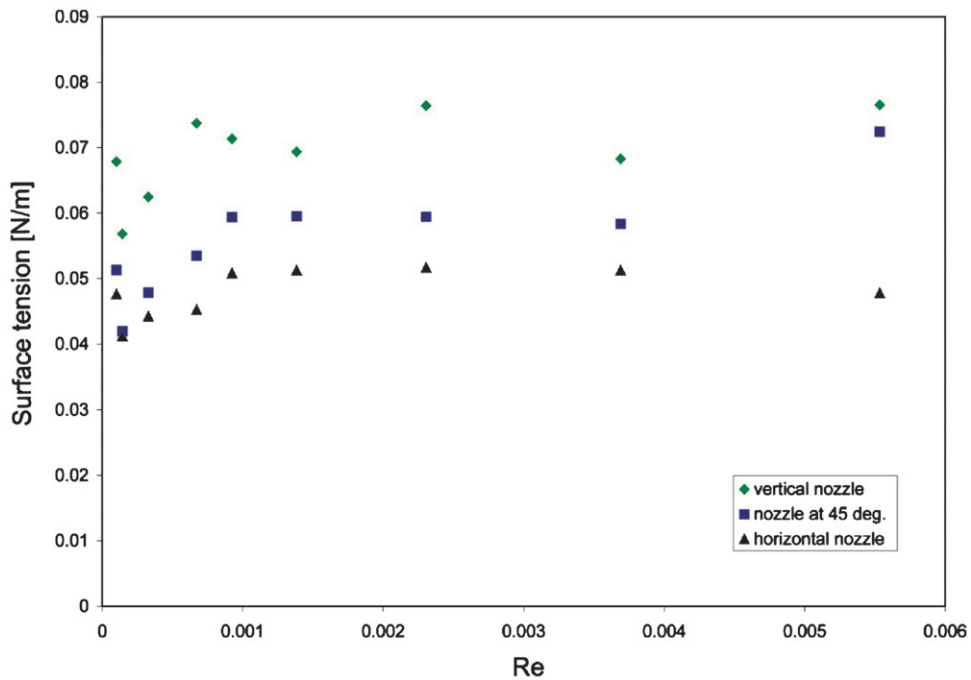


Figure 9. Surface tension, measured with the drop weight method and Harkins and Brown correction factors at different flow rates for horizontal injection with 90° tip-angle; nozzle OD: 1.24 mm (water).

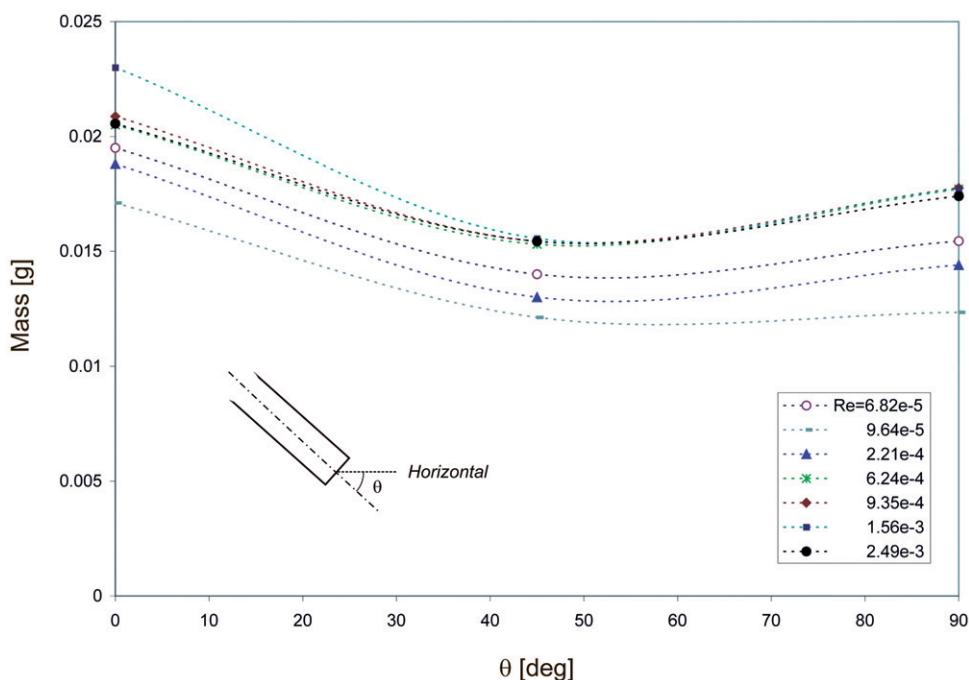


Figure 10. Drop mass vs. angle of a nozzle with 90° tip-angle: horizontal ($\theta=0^\circ$), inclined ($\theta=45^\circ$) and vertical ($\theta=90^\circ$) injection of water from a 1.24 mm nozzle at different flow rates.

value for water, whereas in other configurations the results were underestimated. Similar to Figure 8, for Reynolds numbers less than 5×10^{-4} , there was a decrease in the surface tension coefficient. This was due to the wetting of the nozzle with water; at certain Reynolds numbers, the rate of growth of a drop and the duration of drop formation resulted in water starting to wet the outer diameter of nozzles. It is worth noting that when using the method for solutions, adsorbing molecules will not only change the surface tension of the drop, but also affect its wetting behaviour.

Higher Reynolds numbers correspond to shorter detachment periods and more hydrodynamic effects. For a certain Reynolds number, increasing the angle of nozzle (with constant tip-angle of 90°), from vertical (corresponding to $\theta=0^\circ$; see Figure 10) to horizontal, the drop mass became smaller (minimum at almost 45°). The reason was similar to the case of horizontal injection with different tip-angles. For a 90° tip-angle nozzle, the angle influenced the internal flow significantly. In addition, for positions at small angles, there is a possibility that the wetting of the nozzle be different from the case of a 90° tip-angle nozzle at θ -direction. According to Figure 10, an increase in the angle (towards the vertical position) produced larger drops; hence, the dimensionless radius decreased. The same set of experiments for a nozzle 10% smaller in diameter was performed, and a similar trend in the dependence of drop mass to the angle was observed; however, low Reynolds numbers for this nozzle resulted in less deviation of the flow. Since the diameter was small, the wetting was similar at different angles. Lower Reynolds numbers

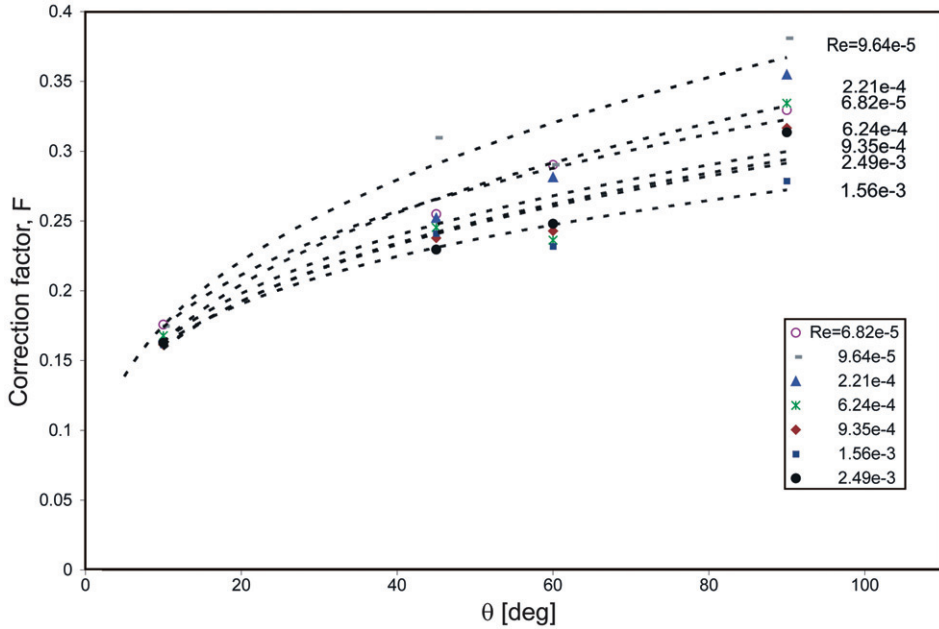


Figure 11. Correction factor vs. angle of injection; horizontal injection of water from a 1.24 mm nozzle.

corresponded to longer detachment times; therefore, water had enough time to wet the nozzle (compared to the conditions at higher Reynolds numbers with shorter detachment periods).

Knowing the surface tension of water from the profile matching method, a new correction factor for the drop weight method was derived from the experiments in horizontal injection from a 1.24 mm nozzle with different tip-angles. As illustrated in Figure 11, in horizontal ejection, the smaller the tip-angle, the less sensitive was the correction factor to the Reynolds number. At larger angles, higher Reynolds numbers resulted in overestimation for the surface tension (i.e. smaller correction factors). In addition, the range of Reynolds numbers studied here reveals that the momentum forces were at least three orders of magnitude smaller than the viscous forces.

4.1. Drop formation; considering the angle of ejection

As noted above, at low flow rates gravitational and interfacial forces are the two dominant forces in drop formation. Therefore, for small Weber numbers (We), the Bond number (Bo) determines condition of experiments. The experiments with the 1.24 mm nozzle corresponded to Weber numbers ranging from 5.25×10^{-14} to 1.57×10^{-10} .

Figure 12 shows the Bond number versus the dimensionless radius for three different configurations; in this figure, the Bond number is different because of the different nozzle diameters used. As shown in Figure 12, the results for the vertical

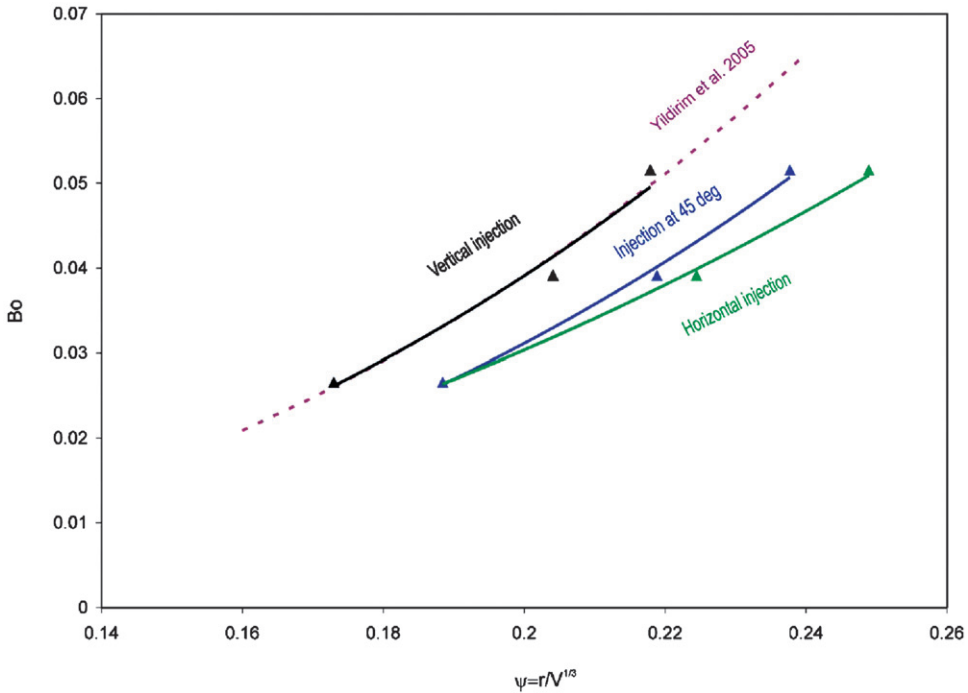


Figure 12. Bond number *vs.* dimensionless radius for different configurations of injection and comparison with results of Yildirim *et al.* [21].

injection agree well with the results of Yildirim *et al.* (2005) [20]; their results were consistent with a dimensional analysis on the parameters governing drop formation. However, since they did not consider injections in directions other than the vertical case, their dimensional analysis was extended to include a parameter for other directions (see Appendix B). Accordingly, a new relation was derived as follows:

$$Bo = 3.37\psi^{2.81} \left(1 - \frac{2\theta}{\pi}\right)^n \tag{8}$$

$$0 \leq \theta < \frac{\pi}{2}, \tag{9}$$

where *n* is almost 0.3. In Figure 12, lines corresponding to different configurations are the best fits on the results for different Reynolds numbers.

The results from Equation (8) were compared with the Lawal and Brown [29] model in Figure 13. The maximum deviation of the dimensionless volume obtained from the model (Equation (8)) with respect to the Lawal and Brown model was about 14%.

4.2. Detachment time of drops; considering the angles of ejection

We considered the angle of injection in measuring the time of detachment in Figure 14. This figure shows the mass of 10 drops detached from a nozzle *versus* the

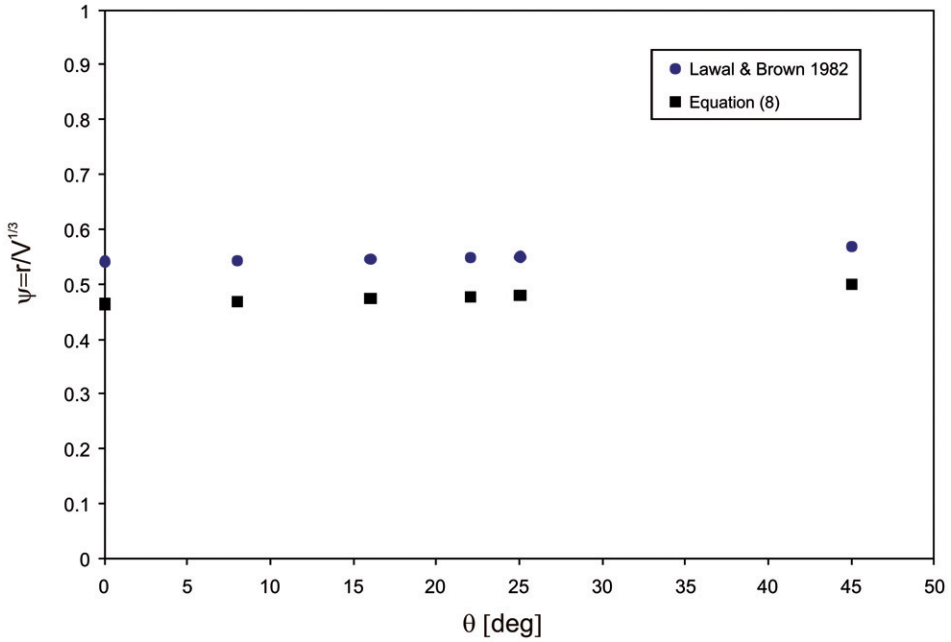


Figure 13. Comparison between the current model (Equation (8)) and Lawal and Brown [29] model for predicting volume of drops for different angle of nozzle. Bond number for all cases is 0.39, and the liquid is water.

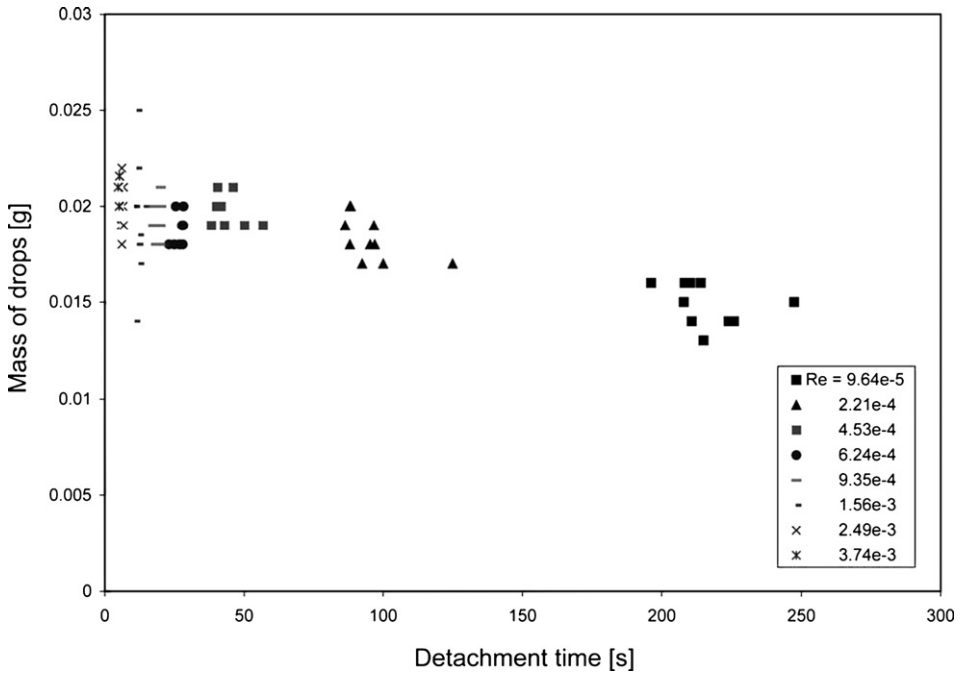


Figure 14. Drop mass vs. detachment time of drops at different flow rates in injection at 45°. For each flow rate, 10 drops were sampled.

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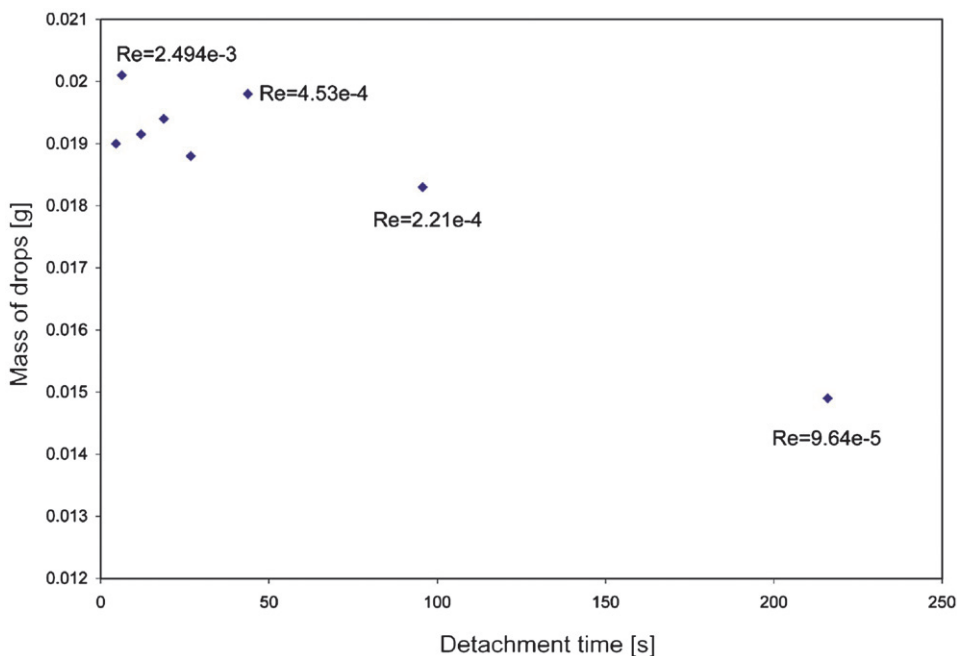


Figure 15. Mass vs. detachment time for injection at 45° from a 1.24 mm nozzle.

corresponding detachment time at different flow rates. As the inertia forces were increased, the drops became larger and detached much faster than the smaller drops. The range of the detachment time for each set of drops with a similar flow rate (i.e. Reynolds number) was narrower for higher Reynolds numbers. At lower Reynolds numbers, the inertial force was not the dominant force and in such a long drop formation period, the influence of different noises, such as vibration in the system due to detachment of previous drops or evaporation, is more conceivable.

Figure 15 shows the general effect of the Reynolds number on the drop mass and the detachment time. An increase in the Reynolds number resulted in larger drops. At Reynolds numbers larger than those shown in Figure 15, an increase in Reynolds number resulted in smaller drops. The results of studies by Henderson *et al.* [12] showed such a non-linear relation also for lower Reynolds numbers.

In order to visualise the variation of the time of detachment with the angle of injection at different flow rates, the detachment time for different nozzle diameters was measured (Figure 16). Miller *et al.* [10] studied the time of detachment of the first drop in vertical injection and suggested the following relation:

$$t = \beta_1 + \beta_2 r, \quad (10)$$

where β_1 and β_2 are 0.0008 and 0.0041 s cm^{-1} , respectively, and r is the radius of nozzle. They also presented Equation (11) which considers the effect of viscous forces.

$$t = \alpha_1 \ln(\eta) + \alpha_2 \quad (11)$$

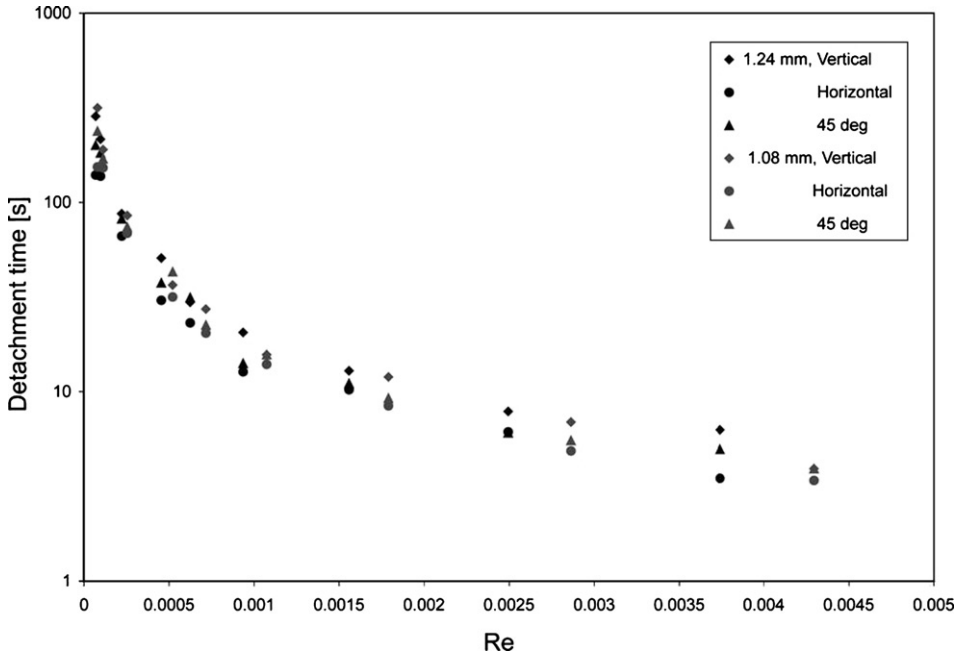


Figure 16. Detachment time vs. Reynolds number for injections at different configurations from two nozzles with different diameters.

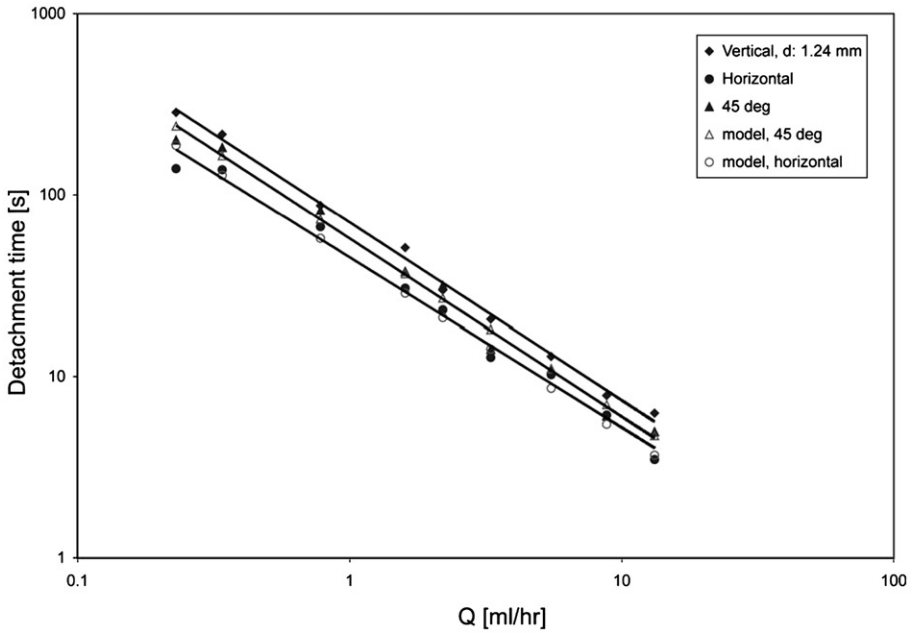


Figure 17. Time of detachment vs. flow rate for injection at three different configurations and validation of the model.

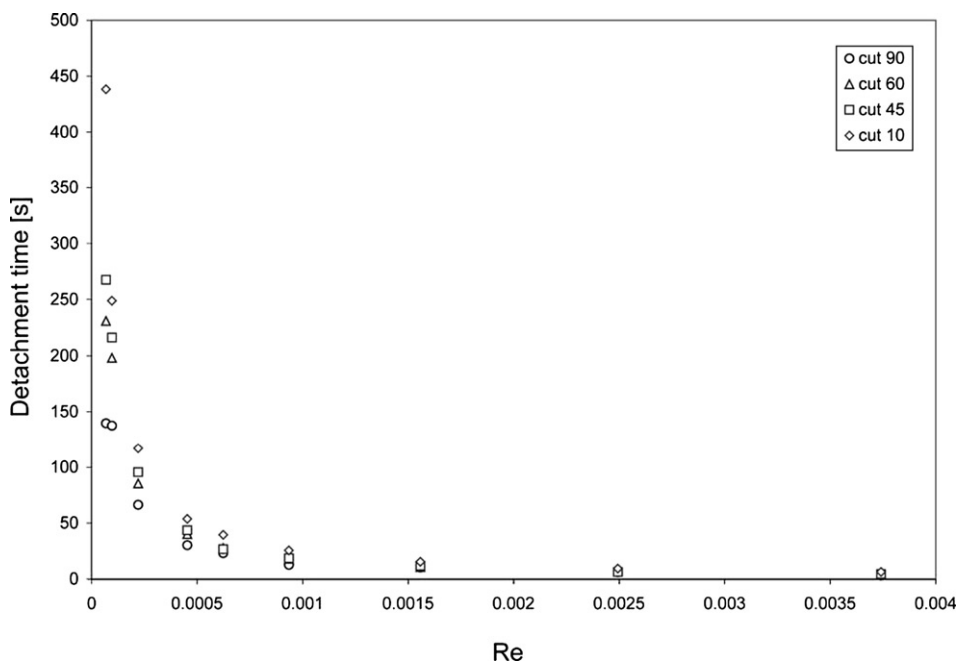


Figure 18. Detachment time vs. Reynolds number for horizontal injection from a 1.24 mm nozzle with different tip-angles.

The coefficients were expressed as:

$$\alpha_1 = 0.0028r + 0.0145, \quad \alpha_2 = 0.0134r + 0.0096 \quad (12)$$

where η is kinematic viscosity ($\text{mm}^2 \text{s}^{-1}$), and radius of the nozzle, r , is in millimetre.

Based on the experiments conducted in this study, a simple model for the detachment time of first drops was derived.

$$t = mQ^p \quad (13)$$

where $p \approx -0.97$; m depends linearly on the angle, and can be expressed by

$$m = \alpha_1\theta + \alpha_2 \quad (14)$$

where in α_1 and α_2 were -16.095 and 70.28 , respectively. To demonstrate the validity of the model, the correlation was compared with the experimental results for the injection at horizontal, inclined (45°) and vertical from a 90° tip-angle nozzle in Figure 17. Errors in predicting the three cases were 1, 1.46 and 4.5% for vertical, inclined (45°) and horizontal injections, respectively. As Figure 18 shows, the detachment time for horizontal injection of water from nozzles with different tip-angles were very similar to Figure 16.

5. Summary and conclusions

The angle of ejecting liquids from a nozzle influences results of surface tension measurements by the drop weight method. The effects of such an angle were

investigated experimentally; new correction factors were derived, and a correlation was suggested to take into account the angle of injection. The correlation predicted experimental results and followed the Yildirim *et al.* [20] and Lawal and Brown [29] results for similar conditions. Although for a routine use of the drop volume methodology, the standard vertical orientation of the capillary remains the recommended way. Hydrodynamic effects were studied to predict the time of detachment for injection at different angles, and a correlation was introduced. The correlation was based on a study by Miller *et al.* [10] for vertical injection considering the angle of injection. Regarding the drop formation, despite much experimental and computational work, more studies on the hydrodynamic effects (i.e. dynamic surface tension measurements by drop weight method) are required.

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Appendix A: Young–Laplace formulation

The geometry of an axisymmetric pendant (or sessile) drop can be presented with a set of ordinary differential equations (Equations (A1)–(A3)) which include different parameters: arc length, s , slope angle of a tangent to a point of the profile, θ and the curvature at the apex, b (Figure 19). The YL equation [25,26] presents such theoretical profiles as a function of the curvatures on two perpendicular planes at each point.

$$\frac{d\varphi}{dS} = \frac{2}{B} - Z - \frac{\sin \varphi}{|X|} \tag{A1}$$

$$\frac{dX}{dS} = \cos \varphi \tag{A2}$$

$$\frac{dZ}{dS} = \sin \varphi. \tag{A3}$$

In Equation (A1), B is the dimensionless curvature at the apex, and $\sqrt{\frac{\Delta\rho g}{\sigma}}$ is used to non-dimensionalise the YP equations.

Appendix B: Dimensional analysis for drop weight method considering the angle of injection, θ

The physical parameters affecting the drop formation due to injection of a liquid a nozzle in θ direction with respect to the vertical direction are as follows:

Volume of detached drop	V
Density	ρ
Surface tension	σ
Kinematic viscosity	μ
Radius of nozzle	r
Flow rate	Q
Gravitational acceleration	g
Angle of the tip with respect to the vertical direction	θ

According to the Π -Buckingham theory, there are four dimensionless numbers governing this phenomenon.

$$Bo = f\left(\psi, We, Oh, \frac{2\theta}{\pi}\right)$$

where $\psi = r/V^{1/3}$ is the dimensionless radius, We is Weber number, Oh is Ohnesorge number and the last term represents the direction of liquid ejecting form a nozzle (θ is shown in Figure 5).

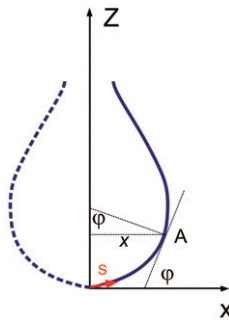


Figure 19. Profile of a pendant drop.