Methyl Ethyl Ketone Spills in Water:
Visualization of the Releases by Optical Schlieren Technique

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Abstract

This study relates to maritime accidents and more particularly to chemical spills from ships stranded in deep water. Marine accidents occurring in France or other countries are important. Many such accidents occurred in the last decade, including the following:

- *Erika* (Bay of Biscay, 1999-2000) containing a cargo of heavy fuel oil in 120 m of water;
- *Luxury* (off Galicia, 2002) releasing 64,000 tons of heavy fuel oil in water more than 3,000 m deep;
- *Ievoli Sun* (Channel, 2000) containing methyl ethyl ketone and isopropyl alcohol in 70 m of water; and
- *Ece* (Channel, 2006): containing a cargo of phosphoric acid in 70 m of water.

All these accidents are due to increasing development of human activities and the economic environment and involve serious toxicological and ecotoxicological effects on maritime fauna and flora and sometimes on the population. When chemical pollution occurs, the population and authorities strive manage pollution faster and more effectively in order to limit its consequences.

It is in this particular and significant context of crisis management of chemical pollution that this study is proposed. This study focuses on a better understanding of the physical mechanisms governing interactions between chemical releases and the environment in order to propose prediction models adapted to the management of marine pollution.

The behaviour of the product in the sea is still unknown as the water solubility or the extent of spill pollution at the surface depends on several factors:

- characteristics of the release (droplet diameter, ascent velocity, trajectory);
- physico-chemical properties of the product (density, viscosity, surface tension, etc.)
- characteristics of the breach (diameter, etc.); and
- environmental parameters (pressure, water temperature, hydrodynamics currents).

This paper focuses on a particular aspect of the project concerning the visualization and characterization of the pollutants released. Some of these pollutants, e.g. methyl ethyl ketone (MEK), are as transparent as clear water and cannot be seen by common imaging systems. To better understand their behaviour in

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clear water (such as blending flows or blending rate), we develop a prototype to control the pollutant release in a clear water cell. Imaging of the liquids blending is reached by strioscopy.

Strioscopy is an optical technique based primarily on the optical Fourier transform obtained in any focal plane of lenses or mirrors. We have designed a Z-mount system with two spherical mirrors so that the optical tank can be placed between the mirrors. The releases are then imaged by a high-speed camera coupled with a relay lens and the real-time spill can be captured at about 2000 frames per second (fr/s). The resulting image clearly shows the presence of MEK and moreover we are able to show the dissolution smear down the ascending spilt drop.

In the future, the whole film will then be analyzed using appropriate image processing to track the droplets and measure the droplet size evolution versus spill time. We will also apply this method to well-known products to enable the generation of an empiric dissolution behaviour library for several substances and compare these results to simulation.

1 Introduction

The maritime route is a primary way of transportation and is constantly increasing. For example, the transportation of chemicals has increased by 270% from 1975 to 1995. As a result, the probability of accidental releases of chemicals is also increasing. For example, 20% of the world's marine transport takes place in the English Channel, which is one of the busiest seas in the world and during the last decade many accidents occurred here.

This fact induces the necessity to better understand the behaviour of chemical releases at the sea surface and also from a shipwreck. This paper concerns this latter aspect. Indeed, in the case of a floating product released from a depth, the physico-chemical mechanisms appearing as the product makes it way to the surface, such as the rate of rise and of solubilization, are still poorly understood, although these parameters influence the extent of pollution at the surface.

For example, we can mention the sinking of the *Ievoli Sun* in 2000 and of the *ECE* in 2006. They both sunk with their noxious cargos: the *Ievoli Sun* carried 4000 tonnes of styrene and 1000 tonnes of methyl ethyl ketone (MEK) and the *ECE* sunk with 10,000 tonnes of phosphoric acid on board. The lack of knowledge about the behaviour of chemicals at sea can be dangerous for people. During the *ECE* accident, French Navy divers were exposed to the acid because it did not dilute as the literature predicted that it would. During the *Ievoli Sun* accident, small leaks of styrene were observed underwater which rose to the surface and exposed people in charge of the intervention to styrene emanations. Moreover, the presence of MEK in the cargo would have led to disastrous consequences. Indeed the MEK has a lower density than water and is not completely soluble in water. So if it is released from a depth, it would rise quickly to the surface and form a slick at the sea surface. The evaporation rate of this product is very high and the cloud is an explosive one. In this respect, this behaviour should be well understood by responders on scene.

That is why methyl ethyl ketone (MEK) was studied by Cedre. The most important difficulty encountered was the MEK droplet visualization in the sea water column. The MEK (as most chemicals) has a refractive index close to the water index, which causes major problems for the assessment of concentrations in the water column and to obtain the rates of rise of the product. Thus this paper concerns

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a specific method to visualize transparent chemicals in seawater based on the optical schlieren technique. Pure ombroscopy will also be investigated, while using dyes with classical photography has not been considered as the dye will flow into the whole seawater column facility. Moreover, we try to develop a mobile non-invasive measurement system that can be used onboard small submarine robots for final measurement application. The final setup will carry the optical imaging system and also the illumination source and lenses.

2 Visualization Technique

We first used the Cedre Experimental Column (CEC) (Figure 1) to visualize spills of different products with classical imaging system, i.e., video cameras (Le Floch et al., 2009). At the very first stages, the illumination and observation modes are done by ambient light. Some products, such as hexane, are very easy to detect in the water and good quality images can be recorded with standard video rates.

Figure 1 Cedre Experimental Column

To enhance the image quality and the visualization of the spill, however, high speed scientific cameras have also been used. This kind of camera enables the choice of the best suited optics and also the setting of all the recording parameters manually, such as recording rate, gain, contrast, and also image size. This is a huge advantage compared to standard video cameras where these parameters are not often easily reachable from the hardware itself. We used AVT Pike camera with video rate of about 200 frames per second (fr/s) for standard 640*480 pixels image area; the smaller the image size, the faster the frame rate. Optics have been chosen to cope with the desired 40*30 cm region of interest (Figure 2).

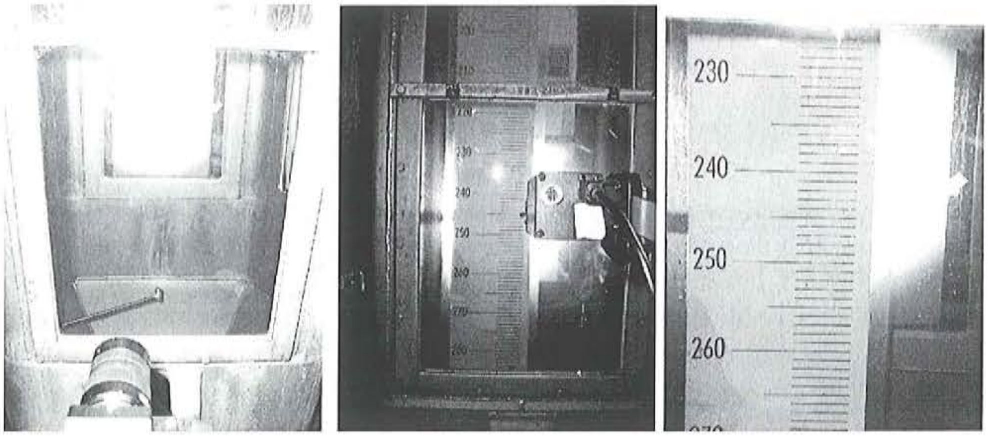

Figure 2 Global Scene and Field of View, in millimetres

To enhance the contrast of the object scene and avoid glare spots, the spill is backlit with a slide projector light bulb impinging on an optical diffuser affixed to the column observation window (Figure 3). As shown in Figure 3, the hexane spill is well imaged with 200 fr/s frame rate.

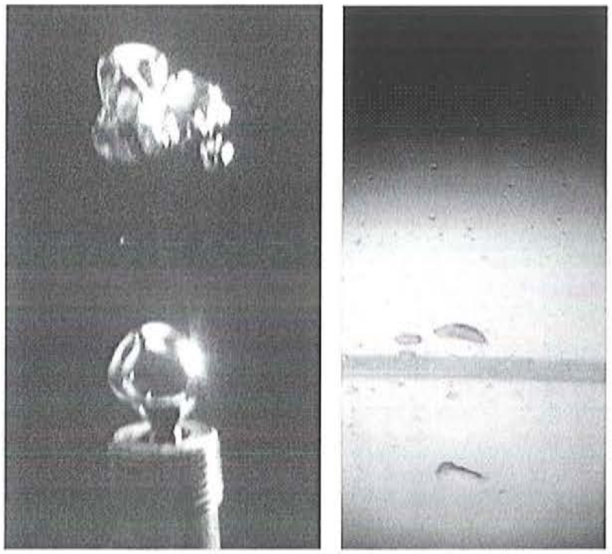

Figure 3 Front Side Illumination and Backlit Drops of Hexane

After the spill release, we can track the spill's upward displacement with a lab-made tracking algorithm. Basically this algorithm is dedicated to detecting grey level changes in the images and with some threshold procedures is able to detect and follow different particles in the same image and to measure size and evolution, as shown in Figure 4.

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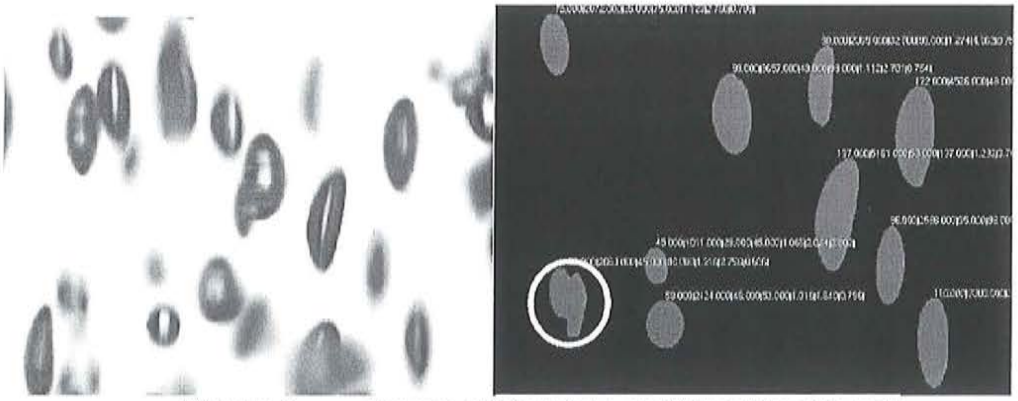

Figure 4 Image of Droplets and Tracking Result

For some kinds of pollutants such as methyl ethyl ketone (2-Butanone, mainly used in the surface coatings industry as resins and nitrocellulose lacquer solvent) with refractive index similar to that of water ($n_{MEK} = 1.3787$, $n_{water} = 4/3$), it is very difficult to distinguish the different liquids with a classical imaging setup. In our setup, we just point out the presence of MEK passing across the column at the diffusing screen boundary. This is mainly generated by the so-called strioscopic effect linked to optical diffraction perturbation at the side of an optical aperture.

The light normally propagating along straight beams must then be considered as a wave front propagating perpendicular to these straight beams (optical rays). Each point encountered by the optical wave front then generates secondary spherical wavelets propagating from these sourcelets in a limited range of directions spanning the direction of propagation of the initial wave front. This is known as the Huygens-Fresnel principle. This principle can be used at the side of our screen where the change of refractive index due to the presence of MEK is then slightly changing the propagation direction of the light. It is then possible to detect the presence of MEK in the water (Figure 5), although this is not clear enough to proceed to measurement of the spill drops.

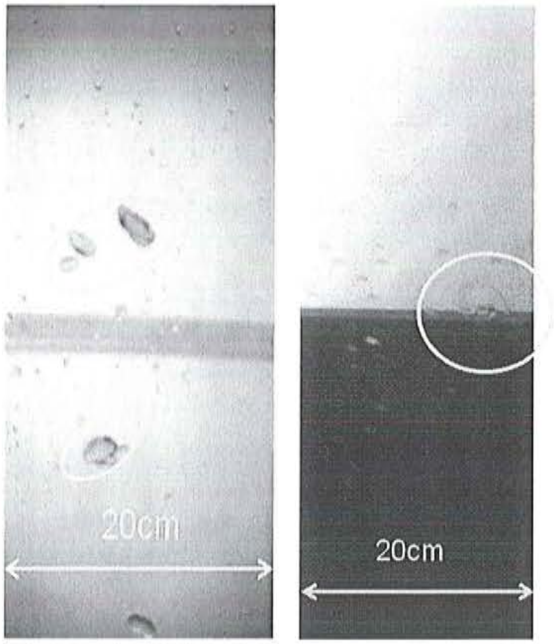

Figure 5 Backlit Drops of Hexane and MEK

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To enhance this phenomenon, we developed a Foucault's strioscopy or schlieren setup (Settles, 2001). The Z-fold configuration is much appropriated for observation through an optical vessel, as the CEDRE water column facility. The first prototype has been designed for laboratory experiment in the optical room and is shown in Figure 6.

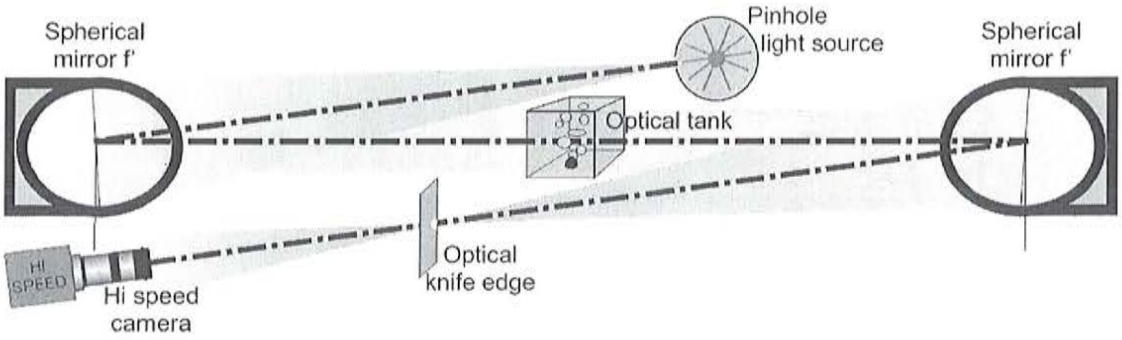
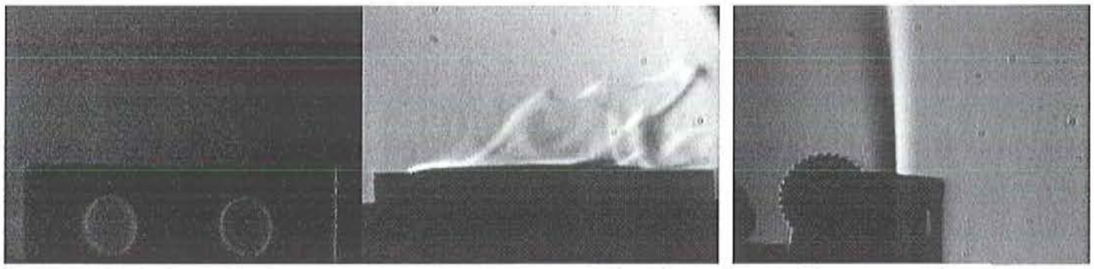


Figure 6 **Two Mirror Z-folded Strioscopy (Schlieren)**

A tiny aperture light source is realized with an automotive light bulb coupled with a pinhole about 400μm in diameter. The pinhole is placed at the focus of the primary spherical mirror to generate a parallel beam of light impinging on the target objects.

Then the secondary spherical mirror back focus the light on the optical knife edge located in the focal plane of the secondary mirror. All the components have to be gently aligned to produce high contrast and good quality images. When the knife edge (e.g. a black painted cutter blade) is placed on the bright focused light spot it is blocking the optical beams coming from the light path in between the mirrors. This set-up also acts as a Fourier transform correlator and the knife edge as the optical frequencies filter. We can then block the low order light (bright spot, no perturbation) and let pass the higher orders generated by optical change in the parallel path. The optical changes can be generated by the physical contours of an object or by refractive index changes in the optical vessel (Figure 7). These images have been captured by the high speed camera focused in the region of interest.



Rectangular bulk and holes contour Acetone evaporation flow Lighter gas outburst

Figure 7 **Strioscopic Images for Object Contouring and Refractive Index Changes**

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In our study, we placed an optical tank filled with water in the optical vessel and then the MEK flow was generated from a syringe pin. The image in Figure 8 clearly shows the MEK drop as a dark object moving in the bright field. Even the dissolution smear can be detected with this setup configuration.

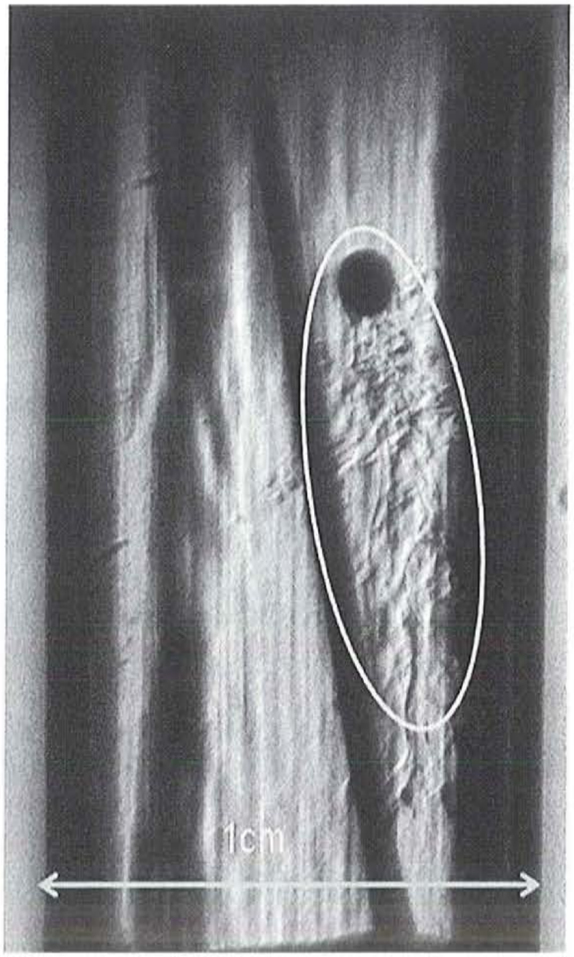

Figure 8 Ascending MEK Drop and the Dissolution Smear

We have successfully applied our tracking algorithm image by image to the recorded high speed movie. The analysis is reached in some tens of seconds and generates a spreadsheet file for further presentation.

3 Results and Discussions

As observed by looking at the movie at reduced speed, the spill drops are first following the syringe and then are leaving this "friendly" environment to go upward in the water. The mean diameter of the droplet is about $1.16.10^{-3}$ m and the mean rate of the spill upward stroke is about $8.2.10^{-2}$ $m.s^{-1}$.

Figure 9 presents the trajectory of the droplet after the tracking process. It is clearly seen the droplet leaves the syringe MEK surrounding and then evolves straight upward (second slope on the propagation curve).

Figure 10 presents the evolution of the MEK bubble velocity versus time. It noticed two zones with different velocity. The first part shows an acceleration of the bubble and then an increase in the velocity that reaches a mean value of 8.2.10-2 m.s-1. The second part shows a constant velocity and represents the terminal velocity of the bubble.

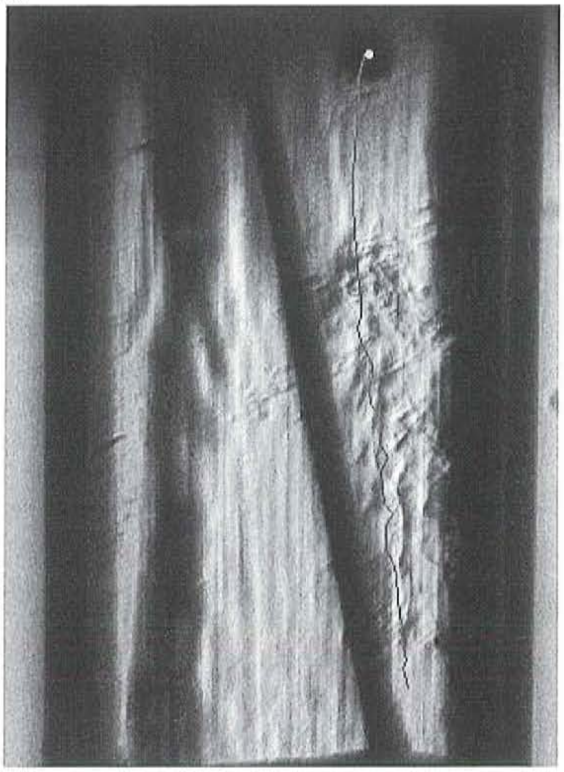

Figure 9 **Ascending MEK Trajectory After Tracking Process**

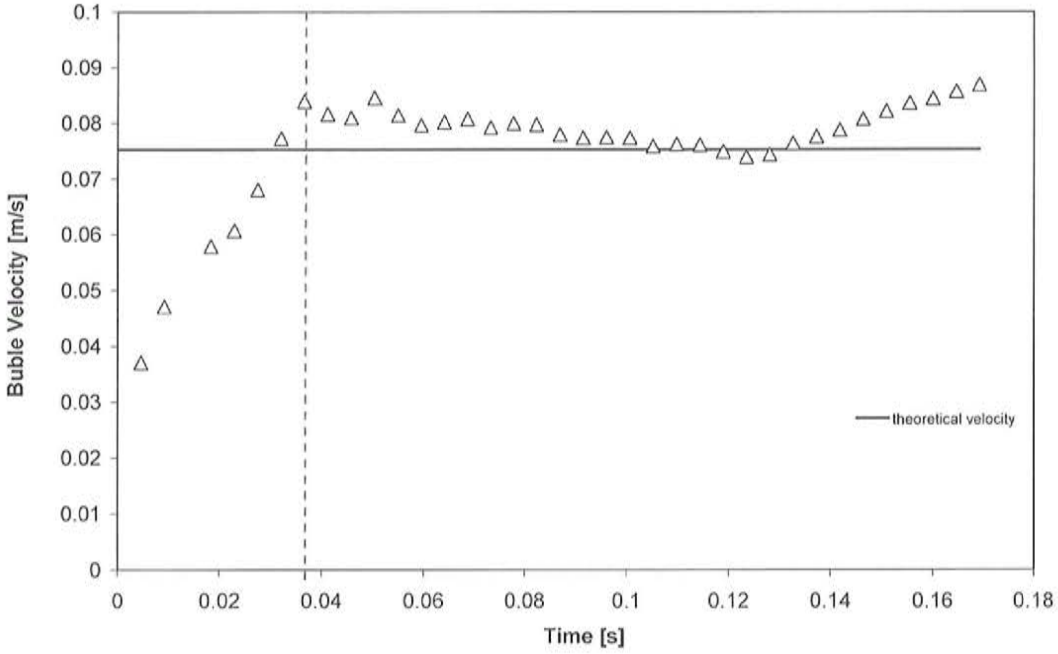

Figure 10 **Evolution of the Bubble Velocity vs. Time**

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Assuming that the droplet of MEK is a spherical particle of D diameter, moving in a stationary fluid, the droplet motion is governed by a driving force due to gravity and a resisting force corresponding to the drag due to relative movement of the droplet in the fluid. According to the Newtonian law (Cloete et al., 2009; Rew et al., 1995), the motion equation is :

$$\frac{du}{dt} = g\left(1 - \frac{\rho w}{\rho_{MEK}}\right) - \frac{3}{4}\frac{\rho w}{\rho_{MEK}}\frac{C_D}{D}u^2 \qquad [1]$$

With u the droplet velocity, ρ_{MEK} the MEK density, ρ_W the water density, C_D the drag coefficient and D the particle diameter.

The rising of a bubble is strongly influenced by its shape. According to the video, we assume that the droplet has a spherical shape that implies a drag coefficient of 0.44 and a theoretical terminal velocity for the droplet of 7.53.10-2 m.s-1. The comparison between experimental data and theoretical value presents a good agreement with a discrepancy less than 10%.

4 Conclusions

This paper presents a new optical methodology to visualize chemical products with a refractive index close to water. This technique allows the velocity and the diameter for a rising bubble in a static fluid to be measured. Moreover, it is possible with the strioscopic method to visualize the solubility of chemical products in water. A first approach based on the Newton law to calculate droplet velocity shows a good agreement between experimental data and theoretical value.

Future work is now focusing on scale factor and development of the spill release control apparatus to produce a well-known spill release in the optical vessel allowing this apparatus to be placed on the optical bench. We will then validate this prototype and transfer to the experimental setup of the CEDRE. A comparison with pure ombroscopy will also be carried out.

5 References

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