

Chemicals Behavior in the Seawater Column

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Abstract

The rapid development of maritime traffic, particularly for economic and ecological reasons, increases the risk of accidental water pollution. This means of transport continues to increase on two points: traffic and capacity. Among the latest accidents, many have led to vessels sinking (Ievoli Sun, 2000 – ECE, 2006).

When a wrecked tanker releases chemicals, it is important to obtain the different quantities of dissolved, floating and evaporating parts to accurately determine the impact on humans and marine environment. Chemical behavior after a release from the deep sea depends of many variables: the mass flow rate at the breach, the distribution of droplets size, the rising velocity and the dissolution kinetics of the products. Moreover, the whole variables are related to physico-chemical parameters of the chemical release (solubility, viscosity, interfacial tension...)

This paper deals with experiments achieved with the *Cedre* Experimental Column (CEC- 5 m high and 0.8 m in diameter of seawater). Several floating products have been investigated. The study of the products velocity during the transfer to the sea surface versus the dissolution kinetics has been performed. Shadowgraphy allows to see transparent chemical in seawater as the refractive indices are slightly different. This technique is based on deviation of parallel light beam through the water column. High speed imaging device is coupled with image analysis processing to record and to analyze the products rising. Three different behaviors were observed for the whole study: products with low solubilization flowing as discrete drops, plume of solubilization drops, and plume of totally miscible product. These results show strong interactions between chemical behaviors versus drag coefficient of the droplet rise and fluid physical properties.

1 Introduction

To date, the international regulations governing the carriage of Hazardous and Noxious Substances (HNS) are based on a theoretical evaluation of the chemical behavior, through the Standard European Behavior Classification (SEBC). It categorizes chemicals on their theoretical behavior following an accidental release at sea. Products are sinker - S, floater - F, dissolver - D, evaporator - E or a combination of two or three of these key behaviors (Bonn Agreement, 1994). This classification contributes to define two major international regulations:

- The IBC Code (IMO, 2007), which defines the type of ship that can carry a given substance;
- The MARPOL classification (IMO, 2006), which assesses the impact of these substances on the marine environment in case of spillage.

The SEBC code is based on physico-chemical properties (density, water solubility and vapor pressure) of substances to determine the typical behavior following a spill. These properties are obtained in the laboratory using standard protocols; for example, solubilization is characterize at the saturation concentration in fresh water, it is measured at 20 ° C and atmospheric pressure. This definition does not take into account the time factor, essential during an accident at sea. Moreover, according to Xie et al. (1997) solubilization in salt water

is about two times slower than in fresh water. Thus the parameters used to classify chemical in the SEBC are far from those encountered at sea during an accident.

If the SEBC may provide an initial answer, operational in charge of the accident must criticize his reading to assess whether the specific environment of the accident will change or not the result.

From an operational perspective, the characterization of the fate of a chemical rising in the water column from depth is poorly evaluated. It requires the determination of certain parameters, including:

- The amount of product dissolved in the water column;
- The amount of product that arrives at the surface;
- The duration of the release;
- The ascent of the product in the water column.

In order to understand the different mechanisms governing the behavior of a chemical in the marine environment, tests were performed with the *Cedre* Experimental Column (CEC). First tests were presented in Fuhrer et al. (2011). They used a light diffuser set-up to visualize drops. In this paper, experiments using another optical method (shadowgraphy) are described. 85 tests were achieved, using 5 chemicals.

2 Materials and Methods

2.1 Experimental Set-up

2.1.1 Cedre Experimental Column

The experimental apparatus is composed of the *Cedre* Experimental Column (CEC) equipped with an injection system and a high speed video recording system. The CEC aims to study the behavior of bubbles, drops or object rising up or falling in a water column (Le Floch et al., 2009). It is a five meter high hexagonal column with a diameter of 0.8 m and a total capacity of 2,770 L (Figure 1). The water in the column is static, it can be fresh or sea water. Four walls are made of glass, allowing observation and video recording within the column.

2.1.2 Optical Set-up

As most of the products are transparent in seawater, a shadowgraphic set-up is used to highlight variations in the refractive index. The set is composed of a collimated source (TZB) aligned on the optical axis of cameras (Figure 1). Cameras 1 and 2 (identical - Table 1) were positioned at the top and bottom of the column to measure the evolution of the different parameters of drops (speed, characteristic diameter, number of elements ...) during their rising in the column.

Table 1: Cameras attributes

	CAM 1 : AVT PIKE	CAM 2 : AVT PIKE
Speed	202 fps	200 fps
Lens	NIKKOR 105 mm	SIGMA 105 mm
Open	2.8	2.8
ROI	640 x 480 pixels	640 x 480 pixels
(Region Of Interest)	33 mm x 25 mm resolution : ~ 52 $\mu\text{m}/\text{pix}$	32 mm x 24 mm resolution : ~ 50 $\mu\text{m}/\text{pix}$

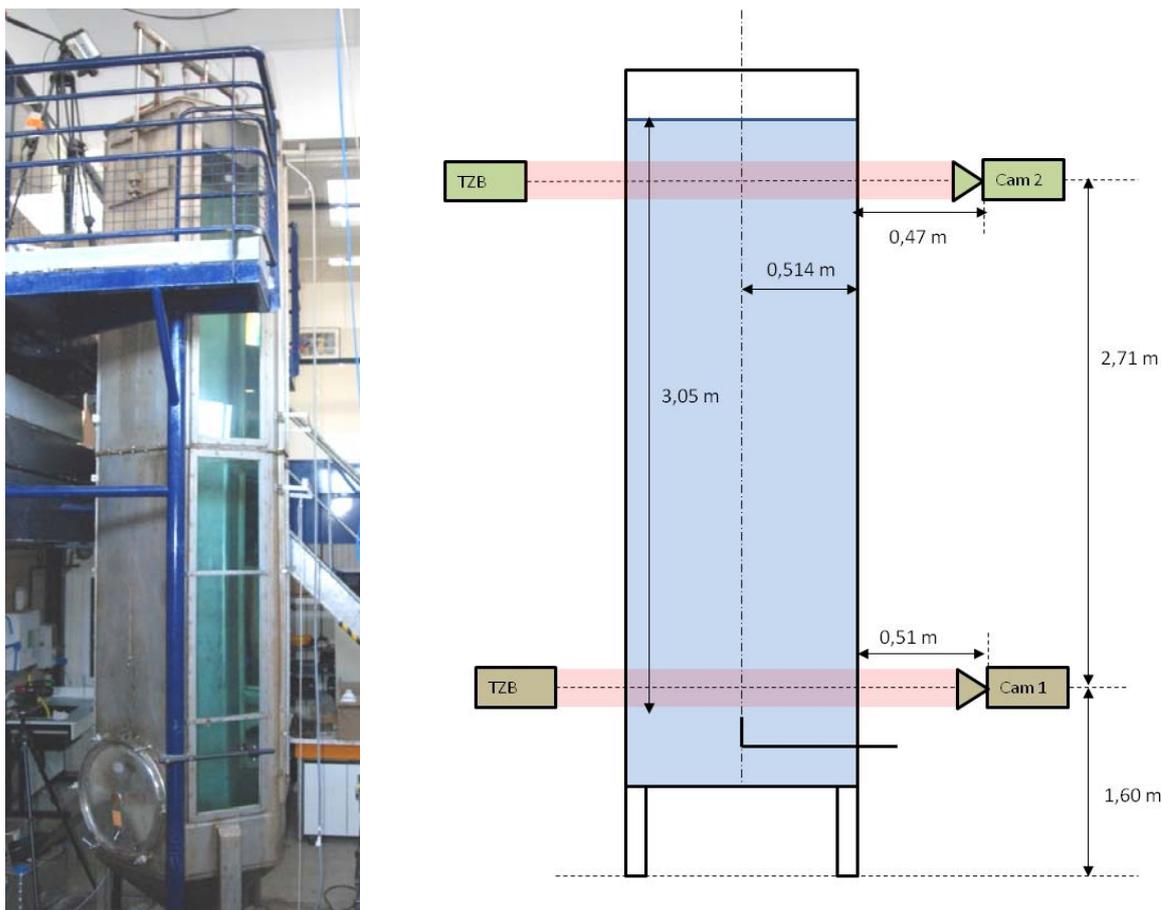


Figure 1: The Cedre Experimental Column and experimentations configuration

2.1.3 Injection

A gear pump (ISMATEC-IP 65 MCP-Z process) equipped with a pump head (Micropump serie 125) ensures the injection of the chemicals at a regular, defined rate. The flow rates tested range from about $300 \text{ mL}\cdot\text{min}^{-1}$ to a minimum value depending on the product to obtain isolated drops.

A 40 cm long injection tube channeled the chemicals into the centre of the column. Two cylindrical nozzles of 7.95 mm and 4.55 mm internal diameter were used during these tests.

2.2 Products

The five chemicals used in these trials were selected for their behavior:

- 2 non-soluble products (Di(2-ethylhexyl)phthalate – DEHP - and Di(2-ethylhexyl)adipate - DEHA),
- 2 soluble products forming drops (n-butanol and Methyl isobutyl ketone - MIK),
- A completely soluble product (ethanol) forming a plume of solubilization and no drops.

Table 2 shows the main physicochemical properties of the products studied. These properties are taken from the database of the ANR project CLARA 2 (Aprin et al., 2011).

Table 2: Physicochemical properties of chemical tested

	DEHP	DEHA	n-Butanol	MIK	Ethanol
Behavior	Non-soluble	Non-soluble	Soluble	Soluble	Completely soluble
CAS number	117-81-7	103-23-1	71-36-3	108-10-1	64-17-5
Density [kg.m ⁻³]	986	930	810	798	783
Hydrosolubility at 20°C [10 ⁻³ g.L ⁻¹]	0,003	0,8	77 000	18 000	790 000
Interfaciale tension at 20°C [10 ⁻³ N.m ⁻¹]	30	-	56 (25°C)	15,7	-
Surface tension at 20°C [10 ⁻³ N.m ⁻¹]	32,2	30,2	25,38	23,6	22,4
Kinematic viscosity at 20°C [10 ⁶ m ² .s ⁻¹]	82,4	14,2	3,8	0,73	1,54

The seawater used to fill the column is taken from the bay of Brest. Before being used it is filtered to remove particles over 25 µm in suspension, and is treated with UV rays (25 mJ.cm⁻²). These treatments prevent flocculation between the substances injected and the matter in suspension so as not to interfere with dissolution kinetics. This seawater has a salinity of 27 kg m⁻³ and the temperature during the tests was between 19°C and 20°C. The refractive index of the seawater is 1.34 (Copin-Montégut, 2002).

2.3 Methods

The image processing is performed using the software Vision Assistant from National Instruments. Particles are automatically detected and analyzed. These analyses consist of the determination of:

- X and Y coordinates of particle center of mass, to determinate drops velocities,
- Equivalent diameter of the particle: diameter of the disc of the same area as the particle.

As same drop appears on about twenty images (depending on the speed of rise), the parameters are averaged to obtain the characteristic parameters of a drop. The drop rising velocity is compared to an empirical correlation usually found in literature: the model for a single drop of Klee and Treybal (1956). It defines terminal drop velocities according to drops diameters, densities of both phases and viscosity of the continuous phase, here the seawater.

3 Results

3.1 Non-soluble Products: DEHP and DEHA

The first results of this experiments set is the increase in the quality of visualization of the droplets with the shadowgraphy compared to previously used light diffuser. Contrasts are high and drops outline are well define (Figure 2).

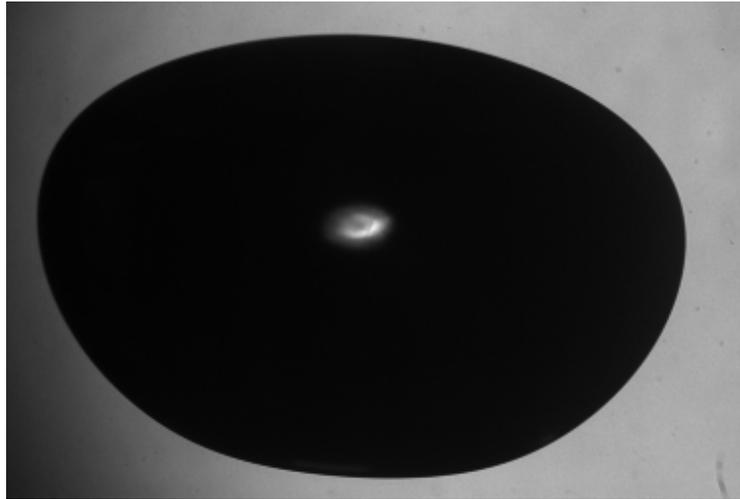


Figure 2: DEHP drop

During the formation of non soluble drops, two types of drops appear (Figure 3):

- Satellite drops of very small diameter (less than 0.4 mm),
- Primary drops of larger diameter (greater than 0.6 mm).

These two sizes of drops can be found on the histogram showing the distribution of drop diameters at the column bottom (Figure 4).

As products are non-soluble, at the column top, the distribution of drops size is expected to be the same as at the column bottom. Figure 5, presents drop size distribution for the same experiments and shows that it is different. However it should be noted that measuring ranges are respected: the DEHA forms drops of 0.1 to 1 cm of diameters.

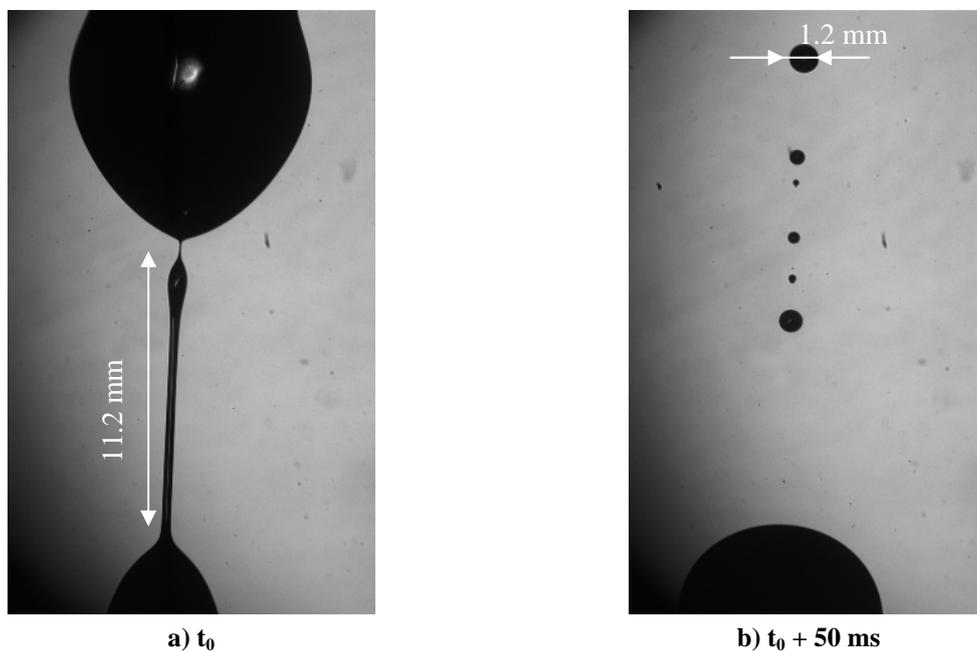


Figure 3: Formation of satellite and primary drops during injection of DEHP

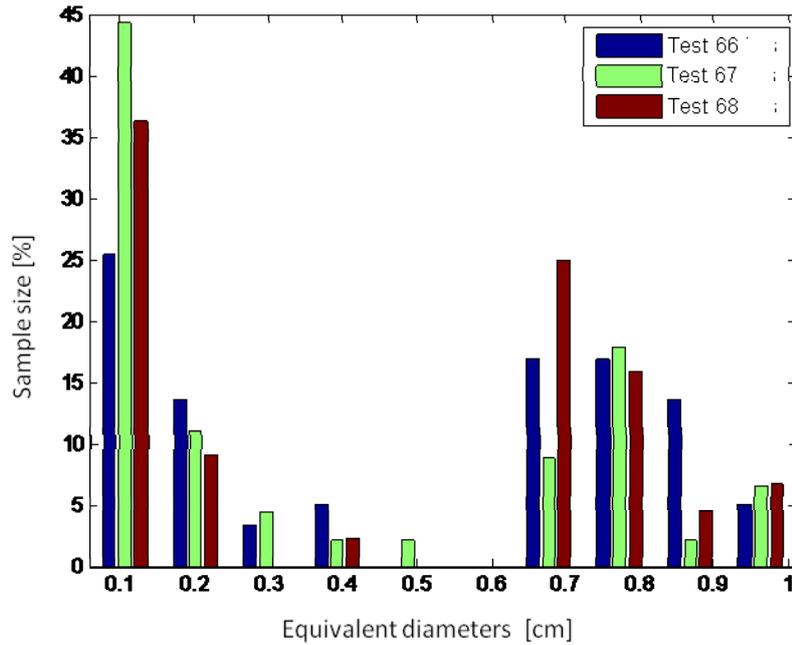


Figure 4: Equivalent diameters distributions for 3 tests in same configuration: DEHA – 190 mL.min⁻¹ – Ø_{inj} = 4.55 mm – CAM 1

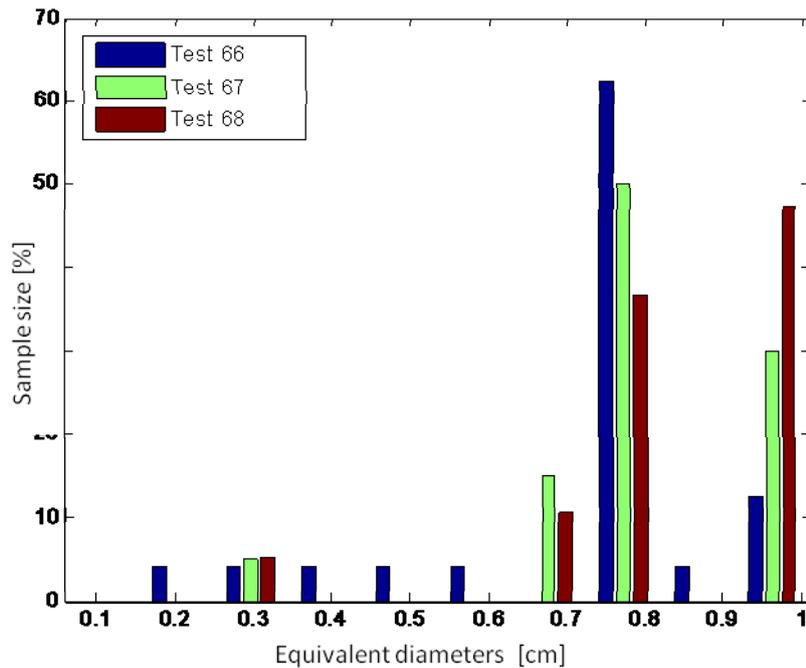


Figure 5: Equivalent diameters distributions for 3 tests in same configuration: DEHA – 190 mL.min⁻¹ – Ø_{inj} = 4.55 mm – CAM 2

Figure 6 shows drops velocities versus drops diameters for all tests of DEHA. This figure brings together all the drops, whatever the experimental conditions (diameter and flow rate injection). The drops of the same test are presented with the same color. The crosses and circles distinguish the drops analyzed respectively in top and bottom of column.

A high dispersion of data can be observed. However, three drops families can be distinguished:

- Group 1: Small drops of diameter less than 0.4 cm, which correspond to satellite drops,
- Group 2: Large drops observed at the top of column,
- Group 3: Large drops observed at the bottom of column.

The theoretical speed proposed by Klee and Treybal (1956) is shown in black line. The behavior of drops of group 1 is very poorly predicted by the correlation of Klee: the measured velocities are much higher than what the model predicts. The large discrepancy is due to the drag effect of large heavy drops that take their satellites in their wake. Their speeds, of the same order of magnitude from those of large drops, do not correspond to the terminal velocity of rise expected for small isolated droplets of the same diameter.

The behavior of large drops is rather well predicted by the theory of Klee, with a significant difference, however, for some measures and in particular for measurements at the bottom of column. This discrepancy is probably due to initial conditions of injection that are not yet compensate for natural dynamics of rising drops and measurement errors due to the complexity of the flow in group.

Thus, these results show so that the velocity of small droplets is strongly dependent on the flow in clusters. The direct application of a correlation of literature established for a single droplet is likely to cause a significant error of prediction of rising dynamic.

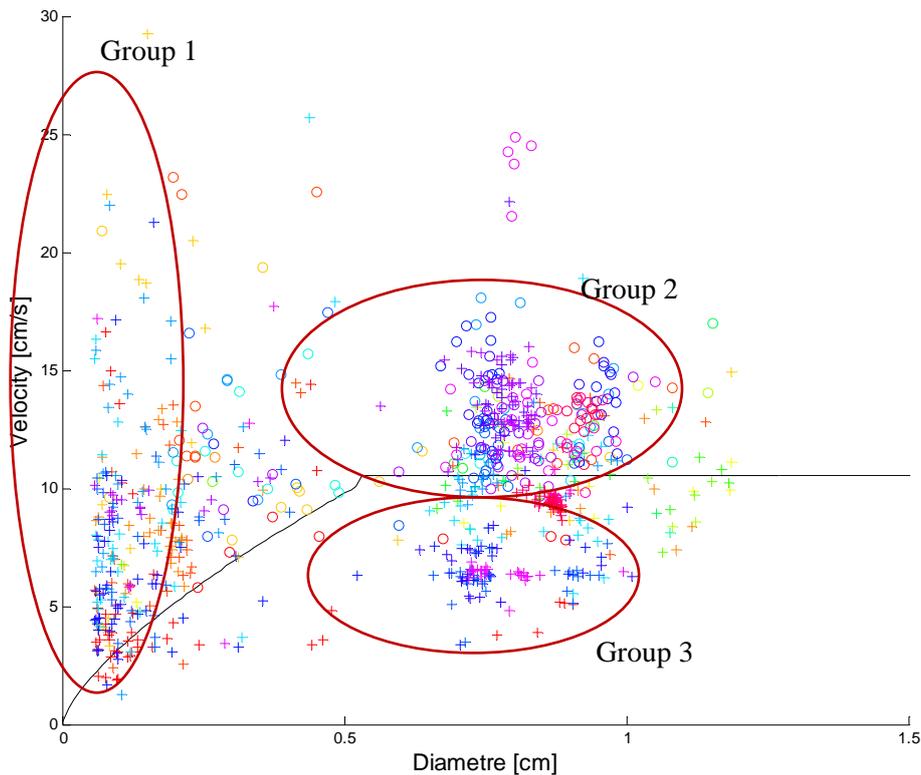


Figure 6: Drops terminal velocity against drops diameters for all test achieved with DEHA

4 Soluble Products: n-Butanol and MIK

As for non-soluble drops, the new optical technique applied during these tests allows to better visualize soluble drops. Drops of butanol show a "cloud" of solubilization. It consists of films detached from the concentration drops which modifies the index of refraction of the medium and displays them. They appear as jellyfish (Figure 7b). The presence of soluble product drops below was absolutely indistinguishable in the previous test campaign (Fuhrer et al., 2011). A trial with light diffuser was performed to compare visualization techniques. Figure 7 shows the images obtained by both methods in the same experimental conditions.



Figure 7: Butanol drops

Released in high quantity, these clouds of solubilization are visible after the passage of drops. They highlight the turbulences and recirculation cells behind the drops (Figures 8 and 9).

At the column bottom and for high flow rates ($> 150 \text{ mL}\cdot\text{min}^{-1}$), both products form groups of droplets of varied sizes. Large structures are particularly visible (Figure 10).

For butanol, at the top of column (Figure 11), these large structures have completely disappeared by fragmentation and small drops were solubilized. The drops have then a smaller diameter distribution but a high uniformity of appearance both for drops and for the clouds of solubilization.

From an optical point of view, clouds left by the passage of drops degrade the sharpness of drops (Figure 11b), which makes analysis more difficult.

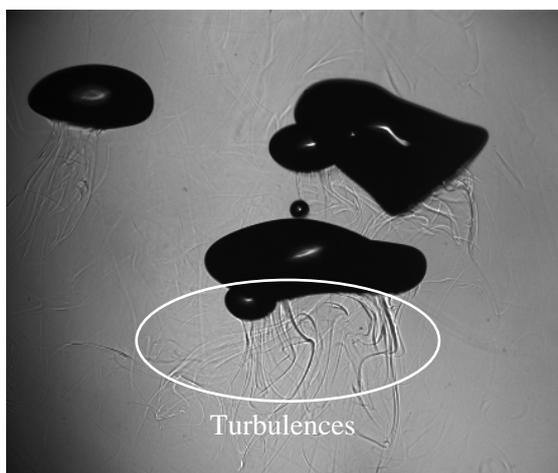


Figure 8 : MIC drop ($180 \text{ mL}\cdot\text{min}^{-1}$ – $\text{Ø}_{\text{inj}} = 7.95 \text{ mm}$ – CAM 1)

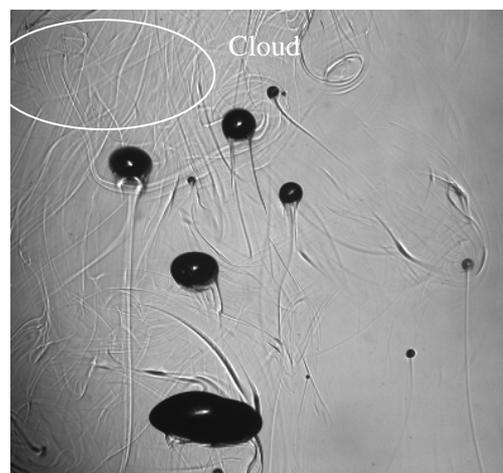


Figure 9 : n-butanol drop ($100 \text{ mL}\cdot\text{min}^{-1}$ – $\text{Ø}_{\text{inj}} = 7.95 \text{ mm}$ – CAM 1)

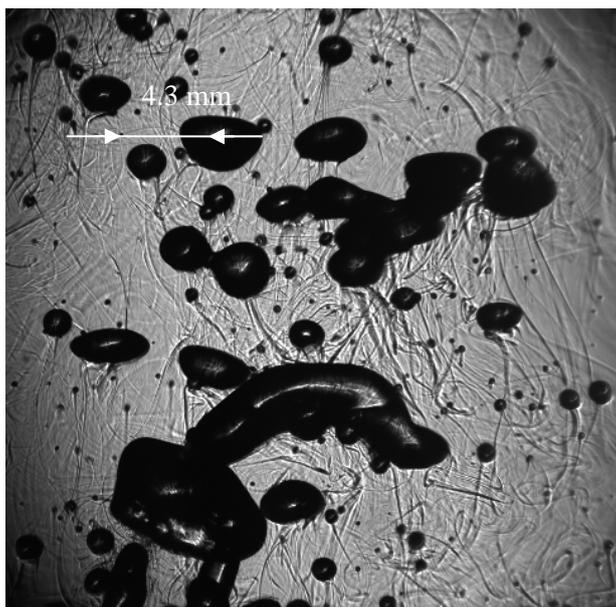


Figure 10: n-butanol drop at the column bottom ($180 \text{ mL}\cdot\text{min}^{-1}$ – $\varnothing_{\text{inj}} = 7.95 \text{ mm}$ – CAM 1)

The compact group of droplets and the clouds of solubilization make analysis of the drops very difficult. Equivalent diameters and velocities could not be calculated for soluble chemicals.

4.1 Completely Soluble Product: Ethanol

Ethanol forms a soluble plume in the water column (Fuhrer et al., 2011). In CEC, the plume is large and as the observation field is small ($\sim 30 \times 30 \text{ mm}$), it is not possible to observe the entire cone of the plume. However, it is possible to see the front of the plume (Figure 12).

Two tests were achieved with ethanol at $300 \text{ mL}\cdot\text{min}^{-1}$ injection rate and the 2 nozzle diameters. Speeds of these plumes are shown in

Table 3. Column bottom and top velocity correspond to front velocity to “cross” the field of view of each camera. These speeds are measured for a displacement of 25 mm. The velocity “through the column” corresponds to front velocity between the 2 cameras for a displacement of 2.71 m.

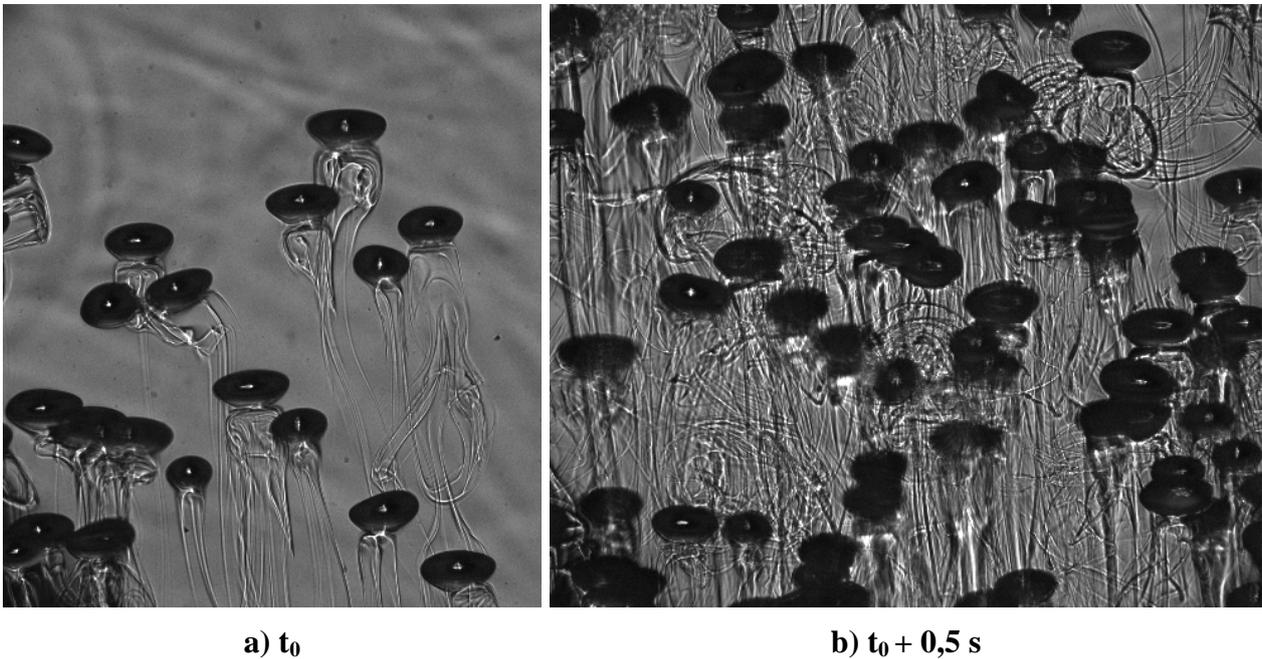


Figure 11 : n-butanol front ($260 \text{ mL}\cdot\text{min}^{-1} - \varnothing_{\text{inj}} = 7.95 \text{ mm} - \text{CAM 2}$)

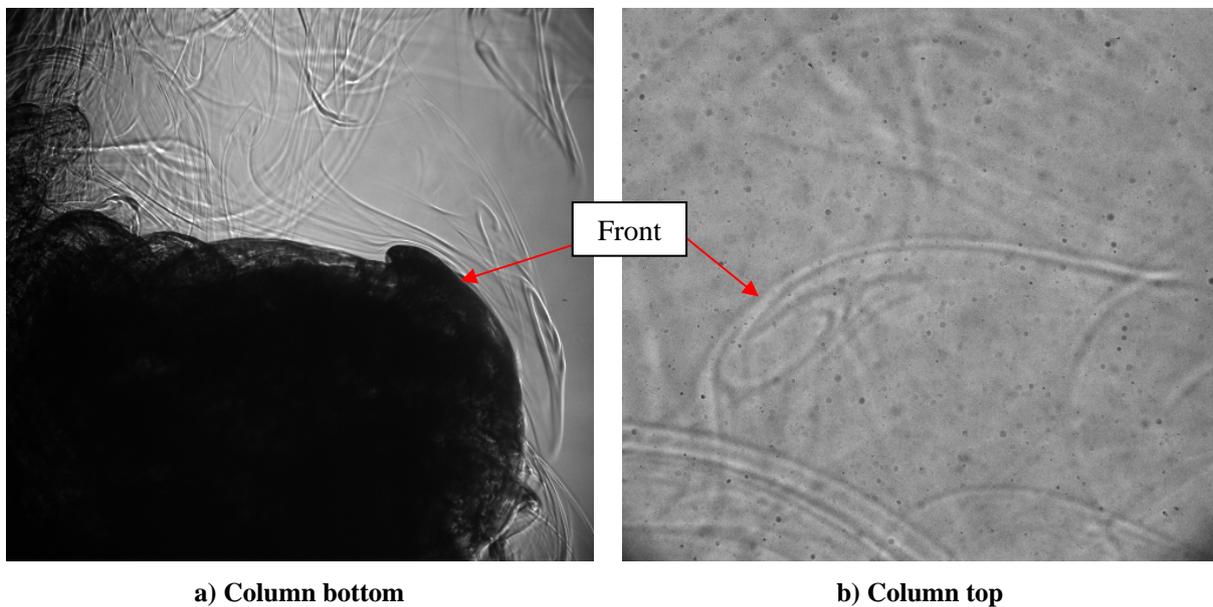


Figure 12 : Front of ethanol plume

Table 3: Velocity of ethanol plume front

	Nozzle diameter [mm]	7.95	4.55
Velocity [cm.s ⁻¹] (± 0.5 cm.s ⁻¹)	Column bottom	5.6	6.2
	Column top	2.0	1.3
	Through the column	2.7	3.0

These speeds are significantly lower than those measured in the case of drops. This difference can be explained easily by the density difference between a drop and a plume. Indeed the density of a drop remains constant and equal to that of the pure chemical whereas a plume is partially soluble and therefore its density approaches that of water then buoyancy is less.

5 Conclusion

This study aimed to model the behavior of chemicals released into the deep marine environment. 86 tests were conducted with five chemicals (DEHP, DEHA, n-butanol, MIC, ethanol) with different discharge conditions (injection rates of 120 to 300 mL min⁻¹, injection diameters of 4.55 and 7.95 mm).

From a metrological point of view, shadowgraphy made high-contrast images and allows to see the clouds of dissolution of soluble substances. The vortex turbulences behind the drops are also visible with this technique. The good quality of images was taken advantage of by an image processing to measure diameters and velocities of many drops.

From a scientific perspective, several points were highlighted:

- The fragmentation of the liquid from a release can lead to two families of disjoint sizes of drops: the main drops, large (up to 1.4 cm in these experiments for DEHP), and satellite drops of size significantly smaller (4 mm);
- In groups, the dynamics of rising drops is generally correctly predicted by the theory of Klee, by cons, large errors can be made on small drops as they are dragged in the wake of large drops and rise faster than the theory prediction;
- The soluble droplets lead to clouds of solubilization which can persist after the passage of the drop. These clouds move slowly toward the surface;
- The liquid completely soluble go back much more slowly than non-soluble drops, a factor of 5 is found.

Future work will focus on different items:

- Another measurements techniques in the case of drops group to improve the dynamic of rise of drops in this context;
- The study of the fragmentation of liquid release from a breach, to determine a typical particle size for a given chemical;
- The study of the solubilization of soluble chemicals in order to take into account the dynamic of rise of drops and their disappearance in the water column.

6 References

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