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# Experimental Analysis of n-Butanol Behaviour in Seawater due to Chemical Release from Marine Shipwreck

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This paper is a contribution to the characterisation of chemicals solubilization in seawater due to marine accident. Experimental tests were performed at large laboratory scale in a large seawater column (CEC) to investigate the mass transfer process for n-butanol release. This column is fitted with glass windows in order to visualize the chemical behaviour in the water column. Experiments were performed with n-butanol at low mass flow rate to perform a droplet flow and to evaluate the solubilization processes at the droplet scale. The mass transfer occurs in the boundary layer which develops on the droplet surface. This solubilization layer detaches from the droplet and generates a persistent cloud of solubilization in the droplet wake. The results on the variation of droplet diameter along the CEC show a decrease of a factor 1.64 which corresponds to a volume loss close to 80 %. Physics of the two phase flow is presented and highlights the solubilization processes in the wake of the droplets with trailing edges vortices. The comparison of measurements with Clift's correlation (Clift, 2005) for droplet rising velocity shows a good agreement for data obtained at the top of CEC but large discrepancies occur at the bottom. This difference can be attributed to the droplet flow regime which corresponds to a non-stationary regime with droplets rising to the terminal velocity.

## 1. Introduction

### 1.1 Maritime chemical transport

Transport by sea highly increased in recent years, due to economic reasons. It is the only solution for low-cost carriage of large quantities over long distances (Cóccola and Méndez, 2013). The transport of chemicals by sea represents 11 % of world trade. Since 1990, these trades were multiplied by 3.5 and the forecasts predict an increase of 16 % by 2015.

This increase in maritime transport generates highly frequented zones between the world's major ports as Straits of Malacca, Singapore, Hormuz and Gibraltar, Suez canals and Panama, Mediterranean Sea, English Channel and North Sea. The combination of these narrow areas with the high density traffic inevitably increases the risk of accidental spills with serious environmental and human damage.

For the European zone and France in particular, the Channel and the Mediterranean sea are two zones of intense maritime traffic. The Channel concentrates 20 % of global traffic and is a necessary passage for ship vessels linking the Atlantic Ocean to the North Sea. Every day, 700 to 800 vessels pass through the Strait of Calais and potentially dangerous cargoes (oil, chemicals, containers ...) is increasing. The number of chemicals transported in bulk rised from 30 Mt/y in 1988 to 150 Mt/y in 2000. Neuparh identifies many accidents due to the important traffic in this narrow area with 86 accidents occurred in the Channel and 70 % involved oil spills between 1960 and 2007 (Neuparh et al., 2012). Moreover, the number of accidents decreases although the volume transported is increasing since 1985. This decrease can be attribute to the improvement of the security transportation (Bahé, 2008). However, since 1990, the number of accidents with chemicals increases and involves new risks (explosion, toxic releases…). The Ievoli Sun sank about 16.7 km from north Casquets by 70 m of depth with chemicals including 3998 tons of styrene, 1 027 t of methyl ethyl ketone (MEK) and 996 t of isopropyl alcohol (IPA) (Law et al., 2003). In addition, the ship

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contained propulsion fuel (160 t of Intermediate Fuel Oil (IFO) and 220 t of diesel). The release quantities from vessel were 400 t of Styrene, 100 t of MEK and 996 t of IPA. This wreck is not the only example of a chemical loss, in 2001 the Balu sank with 8000 t of sulfuric acid in the Bay of Biscay at 4,600 m of depth; in 2006, the Ece discharged 10,000 t of phosphoric acid by 70 m deep. The improvement of the risks management for a tanker accident requires the evaluation of consequences at short term for the rescue teams and at long terms to determine the impact on humans and marine environment (Neuparh et al., 2011). To derive this, the different quantities of dissolved, floating and evaporating parts are required and depends on the physico-chemical parameters of the chemical release, on the marine and weather forecasts (streams, temperature, wind …) and on other variables as the distribution of droplets size or the rising velocity of chemicals. It noticed that many studies exist on spill modelling at different scales (Price et al., 2003, Pallazzi et al., 2004 and Wang et al., 2010).

## 2. Literature survey

### 2.1 Chemical behaviour in seawater

Up to now, the international regulations governing the carriage of Hazardous and Noxious Substances (HNS) are based on a theoretical evaluation of the chemical behaviour, through the Standard European Behaviour Classification (SEBC). SEBC categorizes chemicals on their theoretical behaviour in water, the sinking product (S), the floating products (F), dissolving product (D), the evaporating product (E) or a combination of two or three of these behaviours (Bonn-Agreement, 1994). However, the SEBC code is based on physico-chemical properties (density, water solubility and vapour pressure) of substances to determine the typical behaviour following a spill. These properties are obtained in the laboratory using standard protocols (solubilization is characterized at saturation concentration in fresh water, at 20°C and atmospheric pressure). This definition does not take into account the time factor and meteorological conditions, which are the critical parameters during shipwreck (Le Floch et al., 2010). According to Xie, solubilization in salt water is about two times slower than in fresh water (Xie et al., 1997). Thus the parameters used to classify chemicals in the SEBC are far from those encountered at sea during a marine accident. If the SEBC may provide an initial answer, stakeholders in charge of the accident can criticize its 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 and requires the determination of basis parameters as duration of the release, rise of the product in the water column, amount of product dissolved in the water column, amount of product reaching surface. This paper focuses on the solubilization processes for chemical droplet release in water column (Fuhrer et al., 2012). Figure 1 represents the rising of n-butanol droplet in water. The solubilization process and the mass transfer occur in the boundary layer at the droplet surface which is enhanced by friction and droplet velocity. This solubilization layer detaches from the droplet and generates a persistent cloud of solubilization. Turbulences and recirculation cells behind the drops present coherent structure such as vortex which can be compared to those observed by (Ehara et al., 1993), and obtained with numerical simulation by (Bäumler et al., 2011).

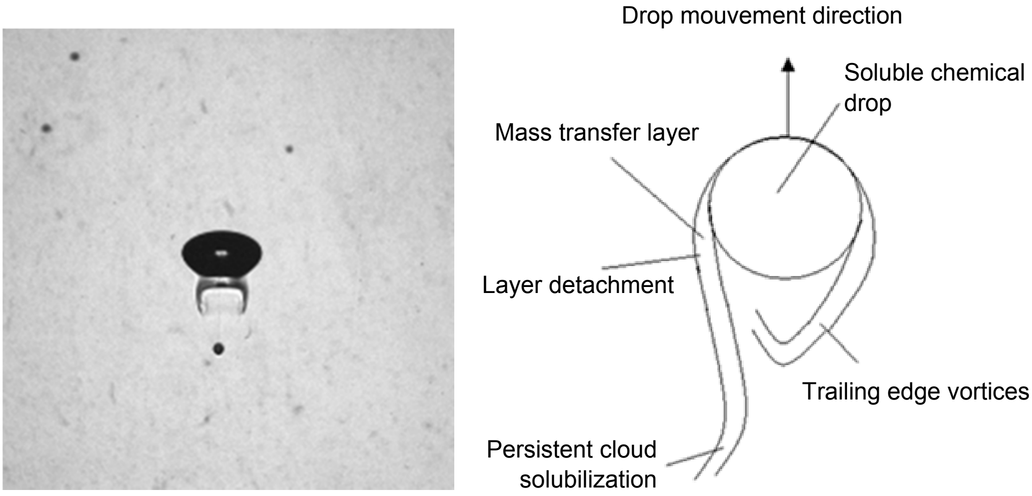

*Figure 1. Illustration of solubilization process for n-butanol droplet rising in seawater. The droplet picture is obtained by Direct Shadowgraphy Imaging technique (Fuhrer et al., 2012).*

## 3. Materials and methods

### 3.1 Description of experimental device

The experimental tests were performed in the Cedre Experimental Column (CEC), which is a 4 m high hexagonal column with a diameter of 0.8 m and a total capacity of 2,770 L. It can be filled with fresh or sea water and is able to study the behaviour of bubbles, drops or object rising up or falling in a water column. CEC is equipped with four full length glass windows to perform observation. The injection nozzle presents a circular nozzle of 4.55 mm of internal diameter and is located at the bottom and at centre of the column. Injection is connected to a gear pump to inject chemicals at a regular and accurate flow rate in a range between 120 mL/min to 300 mL/min. To perform this study, n-butanol was used to represent the chemical release. This product is liquid with a density lower than seawater and it has been selected according to the frequency of transportation, accidents and its hazardous nature. The physico-chemical properties used for n-butanol are obtained by Bertakis (Bertakis et al., 2010) and are listed on Table 1.

*Table 1.Physico-chemical properties of n-butanol*

| | n-butanol |
|---|---|
| Behavior in water | Soluble |
| CAS number | 71-36-3 |
| Density [kg/m3] | 845.44 |
| Hydrosolubility at 20 °C [g/L] | 77 |
| Interfaciale tension at 20 °C [mN/m] | 1.63 |
| Dynamic viscosity at 20 °C [mPa.s] | 3.28 |

### 3.2 Optical set-up

For the present investigation, two different optical devices were used to highlight the variations of droplets refractive index and to measure the velocity and the droplet diameter at different level in the column (Figure 2). A large scale “Edgerton” retro-reflective shadowgraphy system named Pure In Line Shadowgraphy (PILS) is used at the bottom and the top of the column to visualize the droplets flow in the column. This system was initially developed by Edgerton (Edgerton, 1958), and modified by Settles (Settles et al., 2005). A second system based on Direct Shadowgraphy Imaging (DSI) is used to validate the data obtained by PILS. This method is performed with collimated source aligned on the optical axis of middle camera. All the detailed explanations of experimental setup and optical characteristics are presented in previous works (Aprin et al., 2013).

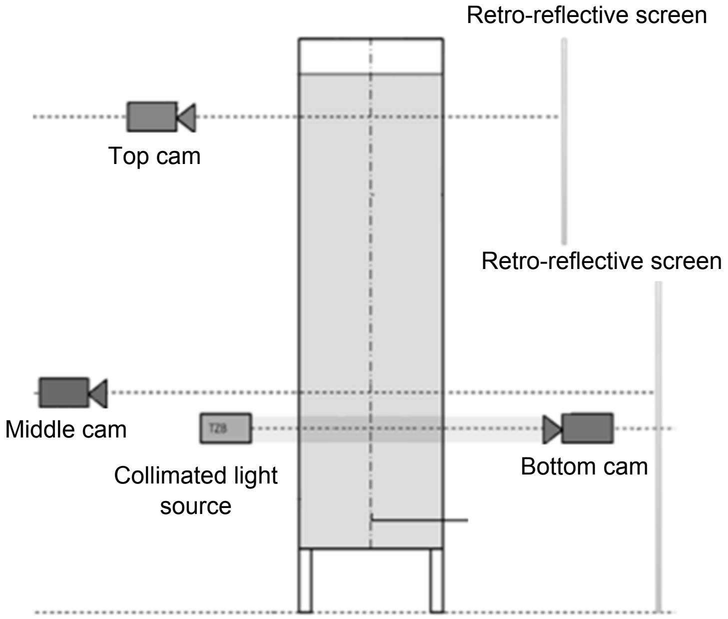

*Figure 1.Position of the optical set-up (Pure In Line Shadowgraphy and Direct Shadowgraphy Imaging)*

## 4. Results and discussion

Figure 2 illustrates the variation of equivalent diameter between bottom and top of the column. The equivalent diameter is obtained by visual measurements and corresponds to the droplets width. Each data represents the variation of mean diameter for the same droplet. These figures clearly show the decrease of droplets diameter between 4.2 mm at the bottom to 2.4 mm at the top. Thus the equivalent diameter is divided by a factor of 1.76 between bottom and top, linked to droplet volume decrease of about 82 %.

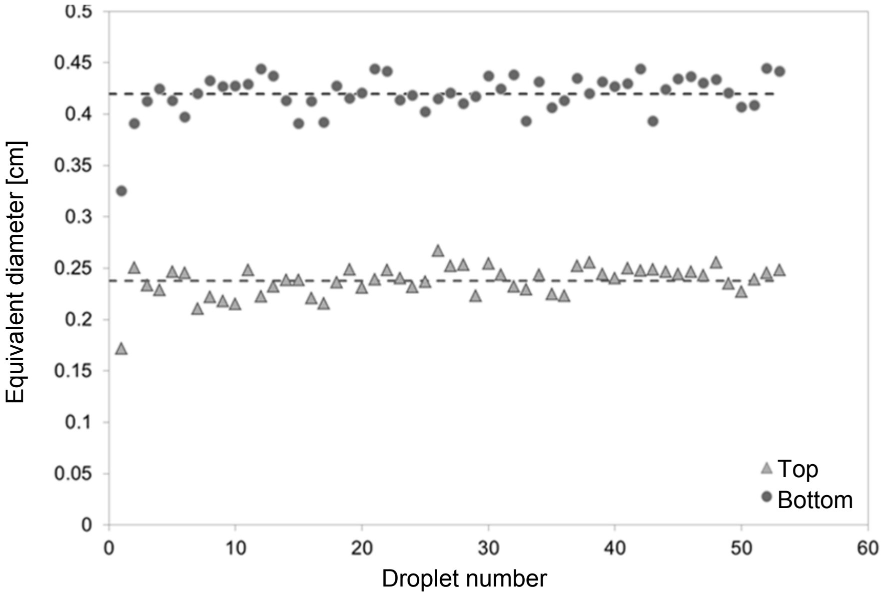

*Figure 2. Variation of equivalent diameter for n-butanol/seawater system between bottom to top of CEC*

Pictures of n-butanol, at the bottom and top of the column are presented on Figure 4. These pictures are obtained from previous works with n-butanol and DSI technique (Fuhrer et al., 2012). At the bottom (Figure 4a), groups of droplets have varied sizes with particularly large structures. At the top (Figure 4b), these large structures have completely disappeared by solubilization and fragmentation, and small drops were entirely solubilized. It has to be noticed on both images that the cloud of solubilization is visible after the passage of drops.

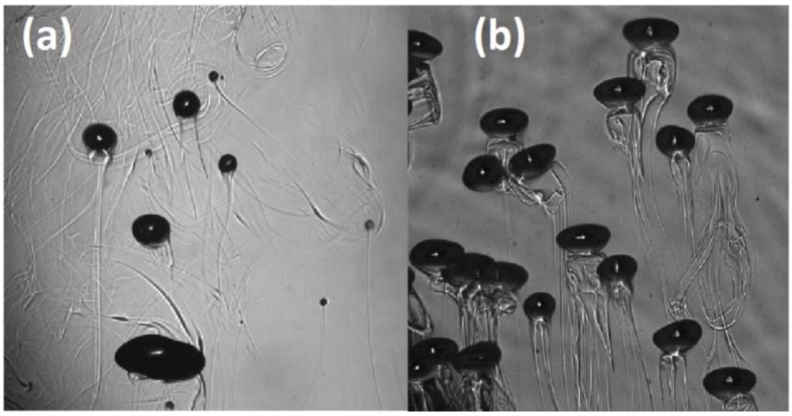

*Figure 4. Images of n-butanol rising droplet in seawater obtained by DSI technique, (a) picture obtained by the bottom camera, (b) picture obtained by the top camera (Fuhrer et al., 2012).*

Figure 3Figure 3 represents the variation of droplet rising velocity between bottom and top of the column and the comparison with Clift's theory (Clift, 2005). Clift has shown the shape of fluid particles could be approximated by a sphere for small size range (smaller than 1mm), an ellipsoid in the intermediate size range (1mm to 15mm), and a spherical-cap in the larger size range. Clift proposed several correlations

depending on the different regimes of droplet shape. For the present study, the regime of ellipsoidal shape is retains because droplets diameters are in the range of 2 to 5 mm.
The droplet velocity for this regime can be derived from:

$$v = \frac{\mu_c}{\rho_c d} Mo^{-0,149}(J - 0,857) \tag{1}$$

Where

$$J = 0,94H^{0,757} \qquad 2 < H \leq 59,3 \tag{2}$$

$$J = 3,42H^{0,441} H > 59,3 \qquad 1. \tag{3}$$

$$H = \frac{4}{3} Eo Mo^{-0,149} \left(\frac{\mu_c}{\mu_w}\right)^{-0,14} \qquad 2. \tag{4}$$

With $\mu_c$= dynamic viscosity of continue phase; $\mu_w$= dynamic viscosity of water ($\mu_w$ =0.9 mPa.s), $\rho_c$= density of continue phase; Mo = Morton number; and Eo = Eötvos number.
Figure 3 is a comparison of experimental data of n-butanol droplet velocity rising in the CEC and Clift's theory. This figure clearly shows a rising velocity in a range between 7.5 cm/s to 10.5 cm/s. The comparison with Clift's correlation presents a good agreement for data obtained at the top of CEC but a large discrepancy exists for those obtained at the bottom. This can be explained because droplets have not reached the terminal velocity at this level.

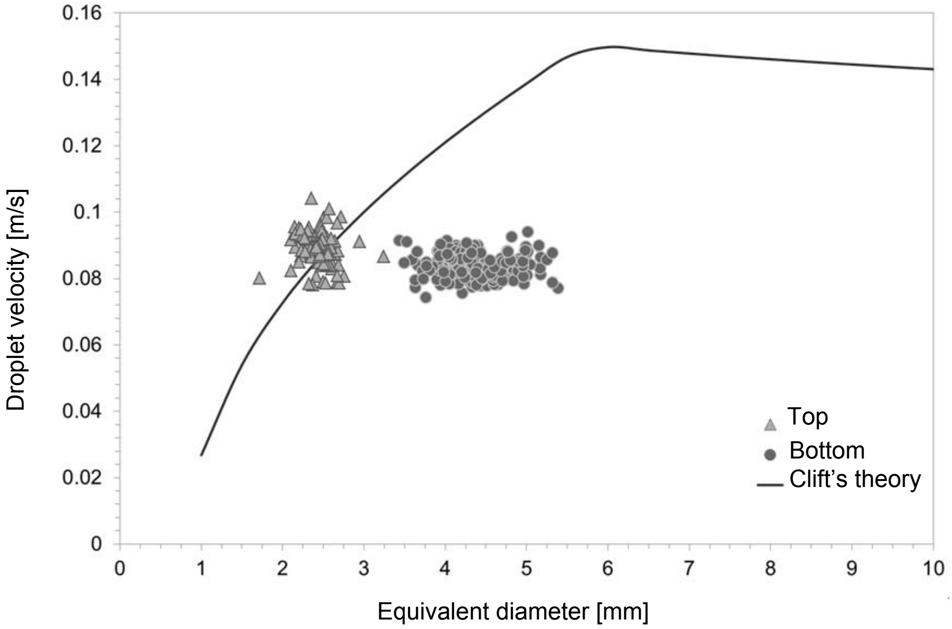

*Figure 3. Variation of rising velocity vs. equivalent diameter at different levels in the CEC, and comparison with Clift's theory.*

## 5. Conclusion

This paper is a contribution to the characterization of chemicals solubilization in seawater due to marine accident. Experimental tests were performed at large laboratory scale in a huge seawater column (CEC) to investigate the mass transfer process for n-butanol release. Two different optical systems were developed to highlight the solubilization process. These experimental devices are obviously well adapted for this analysis and yield to several conclusions. The proposed approached involves a better estimation of the solubilization processes of chemicals in sea water. In comparison with the SEBC method that is performed at laboratory scale with small quantity of chemicals and fresh water, this study is more representative of in-situ release and tends to better estimate the chemical mass reaching the surface. From a global scale, droplet diameters were measured and clearly show a decrease of a factor 1.64 along the CEC which correspond to a volume reduction of almost 80 %. The comparison of measurements with Clift's correlation for droplet rising velocity shows a good agreement for data obtained at the top of CEC but large discrepancies occur at the bottom. Future works will focused on this critical part and will require new experiments with other chemicals to sharply determine the rising velocity and mass transfer rate for massive release, in order to propose a new method ti estimate the consequences for first responders.

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