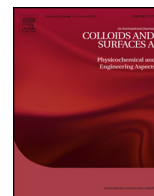




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Bubble adhesion onto the hydrophobic surface in solutions of non-ionic surface-active agents

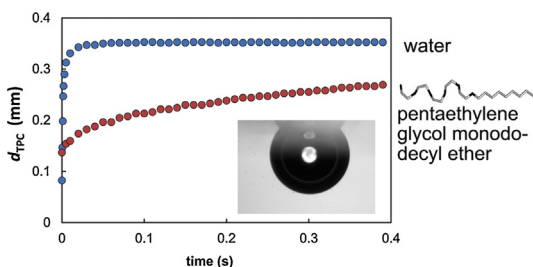
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HIGHLIGHTS

- Bubble adhesion onto a hydrophobic surface was captured using a high-speed camera.
- Three non-ionic surfactants differing in the structure were compared.
- The coherence between TPC line expansion, surface tension and wettability is studied.
- The suitability of non-ionic surfactants as flotation agents is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Bubbles and drops are entities of enormous practical interest since their interfaces are encountered in numerous industrial processes. Froth flotation is just one of the examples in which bubble–particle attachment and especially fast bubble adhesion play a vital role. This work is focused on the experimental study of the three-phase contact (TPC) line expansion during the bubble adhesion onto the hydrophobic surface in solutions of three non-ionic surface-active agents (Terpineol, Triton X-100 and pentaethylene glycol monododecyl ether), which differ in their structure. The diameters of the TPC line together with bubble dynamic contact angles, dynamic surface tension, bubble rising velocity and dynamic drop contact angles were measured. It was confirmed that the bubble adhesion is fast in solutions of such surfactants whose hydrophobic and hydrophilic parts are small. On the other hand, surfactants with long and flexible hydrophobic tails exhibit more complex behaviour which usually leads to slower bubble adhesion. The molecule steric orientation in the proximity of the interface strongly influences the surfactant motion and thus the predictability of bubble attachment efficiency is low.

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1. Introduction

Over the past century, plastics have become an essential material being commonly used in a wide variety of applications due to their lightweight and excellent thermal and electrical insulation properties [1]. Plastics are used for medicinal purposes such as unblocking blood vessels or in prosthetics, in everyday products

including packaging for food and other goods, in the automotive industry, and in sports equipment and safety equipment like helmets or fire suits. The high demand for plastics means a high production rate with an estimated 57 million tonnes being produced in 2013 from the EU-27 alone, while simultaneously producing a high level of waste. By 2020, the EU-27 has set a target of having zero plastics dumped in landfills. This target was set because plastic products at the end of their life are too valuable to discard since they can be re-formed into their original state, utilised to generate heat and power from combined heat and power plants, or used to bolster plastic supplies.

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Of the four stages in plastic recycling: collection, separation, processing/manufacturing and marketing, separation is considered to be the most important as only the highest quality resins can be used for preparing plastic or chemical products. Currently, methods such as gravitational separation, automatic sorting and electrostatic separation are used however each have their own advantages and disadvantages. The EU has invested in developing new methods for the separation of plastics after collection, including smart and green interfaces, to help reach its goal. This method utilises flotation to separate the plastics, an already proven efficient separation method in mineral processing where the attachment of bubbles increases the flotation of some materials while depressing others allowing separation to occur. During flotation, a stable froth has to be maintained above the flotation pulp in order to collect the floated valuable particles. Therefore the surface-active agents are added to the flotation liquid. Surfactants also adjust the required surface tension of the bulk liquid [2–4]. An important aspect of flotation is how the bubbles attach onto the particles and how the surfactants influence the expansion of the three-phase contact line between the bubble and the material for which currently little is known about [2].

Surfactants play an important role in interface science, commonly being used as wetting agents. Wetting agents are substrates that can enhance the ability of a solution to wet a solid surface allowing for easier spreading by lowering the surface tension of the liquid as well as the interfacial tension between the two liquids [5]. According to their structure, surfactants are amphipathic organic compounds that are composed of both a hydrophobic and hydrophilic section. Surfactants can be grouped into one of the following categories depending on the charge group on the head [6]: anionic, cationic, non-ionic and zwitterion.

In water, surfactants have two options to ensure each section interacts with its favoured environment. Firstly, it can arrange itself so that the hydrophobic head is above the water surface while the hydrophilic head is still submerged. Secondly, they can arrange into micelles, where the molecules form aggregates so that the head is exposed to water while the tail points towards the centre of the aggregate interacting with each other. The critical micelle concentration (CMC) is the concentration at which micelles form and any surfactant molecules that are subsequently added will join on to the micelles.

1.1. Bubble adhesion onto the hydrophobic surface

The bubble adhesion onto the hydrophobic particle and the stability of created unit determine the effectiveness of the whole separation process in flotation. It is commonly accepted that the bubble attachment consists of two terms: (1) the thinning of liquid film to a critical thickness where the rupture of the liquid film begins; and (2) the expansion of the three-phase contact line to form a stable wetting perimeter [7,8]. This perimeter is usually named as the three-phase contact line (TPC line). The rupture of the liquid film is a very quick process and thus its description is convoluted. Initially it was assumed that the rupture is connected with the density fluctuations and the TPC contact arises from a hole of a certain diameter in the intervening liquid film [2–10]. According to new findings the existence of nanobubbles attached to the solid surface is crucial [11–13]. After the formation of the TPC line its movement can be observed. Spontaneous movement occurs when the system is relaxing from nonequilibrium to an equilibrium state. In the literature, there are two approaches dealing with the kinetics of the TPC line based either on the hydrodynamic or molecular-kinetic theories. The hydrodynamic approach assumes mainly the viscous shear flow as a dissipative force [14,15] whereas the molecular-kinetic model follows the principles of surface chemistry. The theory is based on the statistical mechanics treatment of

the transport processes of molecules and ions [16] and according to our findings the agreement with experimental data is excellent [17].

From the flotation perspective it is important that the bubble adhesion onto the solid surface is rapid, otherwise the flotation efficiency is low. In pure water, the stable perimeter of the TPC line is formed within a few milliseconds [18]. The surfactant presence may significantly affect the kinetics of this process. The TPC line dynamics could be influenced by the surfactant adhesion on solid–liquid, solid–gas and liquid–gas interphases and also by the Marangoni flow along the bubble surface due to the changing surfactant concentration [19]. This work is not focused on the explanation of the above mentioned phenomena although they will be discussed further. The aim is to compare three types of non-ionic surfactants differing in their structure and try to evaluate the bubble adhesion dynamics in solutions of these surfactants.

2. Experiments

2.1. Surfactants

The surfactants used in this study were α -Terpineol (here labelled as Terpineol, CAS No. 98-55-5), Triton X-100 (polyethylene glycol *tert*-octylphenyl ether, here labelled as Triton, CAS No. 9002-93-1) and pentaethylene glycol monododecyl ether (labelled as C₁₂E₅, CAS No. 3055-95-6). All surfactants were of high purity grade ($\geq 98\%$) from Sigma–Aldrich and were used without further purification. Aqueous solutions of these surfactants with desired concentrations (see Table 1) were prepared by dilution with pure water (distilled, de-ionised and de-mineralised) at 25 °C.

2.2. Material

A silanized glass was used as a model hydrophobic surface. The silanization method is based on the covalent attachment of functional organosilanes to silica or glass. Silanes are believed to react with the exposed hydroxyl groups of silanols on the glass surface and, under optimal conditions, they form a uniform monolayer [20]. In our project the common type of silanized glass was used: the Silanization solution I was supplied by Sigma–Aldrich (5% solution of dimethyldichlorosilane in heptane, CAS No. 75-78-5). The silanization method was applied according to recommendations from the literature [20]. The glass material (microscopic slides) was cleaned in a boiling mixture of sulphuric acid and hydrogen peroxide (1:1) for 1 min, then rinsed several times with distilled water and dried. The slides were dipped into the silanization solution for 24 h, and then rinsed firstly with pure heptane then with acetone and ethanol in order to remove all organic residues, and finally they were dried. The silanized slides were stored in a dry place to avoid contact with air humidity. The surface homogeneity was tested using the AFM method. On clean glass, the maximum roughness reached a height of 60 nm (average 15 nm), and on silanized glass the maximum roughness reached a height of 160 nm (average 30 nm). The measurement was conducted within 1 week after preparation. Contact angles for pure water ranged from 103.1 to 104.3°.

2.3. Apparatus

The experimental measurements were performed in a special glass flotation cell (50 cm height, 8 cm width and 6 cm depth) using the freely rising method. Single bubbles were created by a bubble generator at the top of a thin capillary (inner diameter 10 μm , outer diameter 375 μm) and after detachment from the capillary the bubble rose through the liquid to the solid particle represented by silanized glass placed on a horizontal plane. The process of

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