

Nanobubbles and Surfactants

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Abstract

Nanobubbles and surfactants are two special cases with extraordinary properties that have significantly attracted researchers interest in the recent years. In this paper, the relation between them is investigated in terms of interfacial phenomena. It is shown that the observed decrease in the surface tension of anionic surfactant aqueous solutions in the presence of bulk NBs, can be attributed to the electrostatic repulsive interaction between the electro-steric stabilized NBs and the anionic surfactant molecules. This complex system of anionic surfactant-nanobubble functions as a novel surface-modifying agent that can potentially be used in industries like oil & gas industry, food industry, cosmetic industry, wastewater treatment, surface cleaning and medical applications where surfactant technology is extensively applied.

Keywords: Nanobubbles, Surfactants, Surface tension, Electrostatic repulsion

Lecture

Nanobubbles (NBs) are long-lasting nanoscopic gaseous cavities in aqueous solutions and they are classified into bulk and surface. The primary difference between them is that the former lack a three-phase contact line, while the latter have[1]. As a result, bulk NBs are mobile, whereas the surface are not, and, again, the radius of the curvature of bulk NBs is much smaller than that of surface NBs. According to ISO 20480-1-2017[2], bulk NBs are also called ultrafine bubbles. Bubbles with a diameter on the nanoscale, should dissolve immediately conforming to the Young Laplace equation:

$$\Delta P = \frac{2\gamma}{R} \quad (1)$$

where, $\Delta P = P_{vapour} - P_{liquid}$, γ is the surface tension and R is the radius of the bubble. This equation estimates a massive inner gas pressure for nanobubbles as shown in Fig. 1 and, as a result, the Epstein–Plesset theory[3] predicts that they should dissolve on a timescale of 1–100 ms. However, bulk NBs exhibit remarkable level of stability and longevity. The most popular theory about NBs stability is the electrostatic repulsion theory. Nanobubble interfaces in pure water have been shown to be negatively charged, indicating the development of an electric double layer around the nanobubbles[4], [5] as shown in Fig. 2. The accumulated ions surrounding the bubble surface form a thin layer that functions as a diffusion barrier, decreasing gas dissolution and therefore prolonging the nanobubbles lifespan. This process is known as the ion shielding effect[6], [7]. The external electrostatic pressure generated by the charged nanobubble interface is believed to balance the internal Laplace pressure, resulting in no net gas diffusion at equilibrium and the nanobubbles remaining stable. Moreover, Kyzas and Mitropoulos[8], in their pioneer study, explored the possibility of stabilizing a bulk NB by Brownian motion. It

was shown that a fractal walk under specific conditions may leave the size of the bubble invariant.

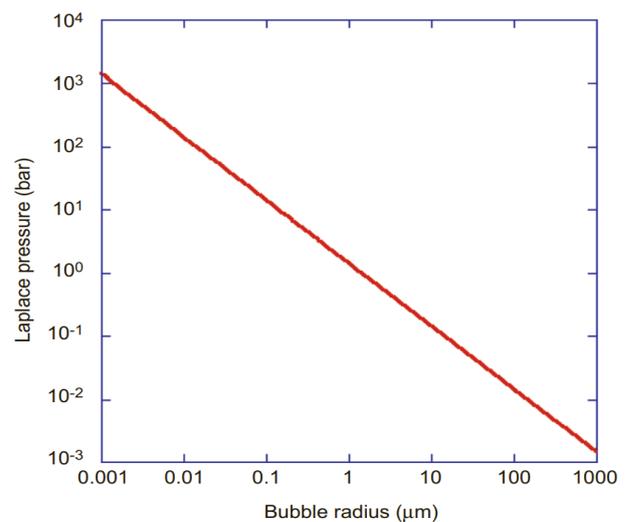


Fig. 1. Laplace pressure vs bubble radius.

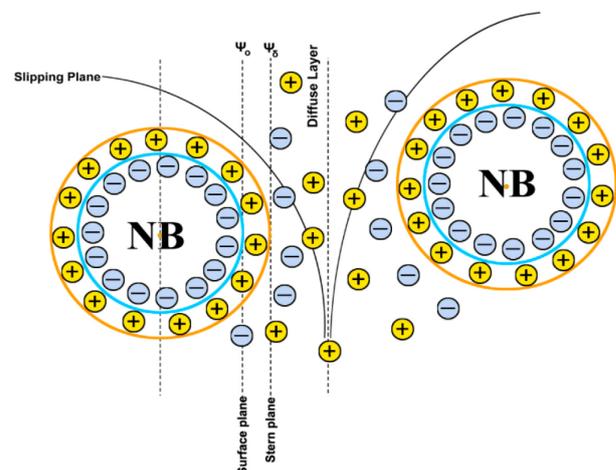


Fig. 2. The electrical double layer for bulk NBs.

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Nanobubbles on water-solid interfaces have been repeatedly observed using atomic force microscopy (AFM)[9]–[11]. On the other hand, NBs cannot be retained at air-water or oil-water interfaces due to their dynamic state and due to the fact that the air-liquid contact line can be pinned at a solid-liquid interface but cannot at a liquid-liquid interface[12]. This explains why no reduction is observed in the surface tension of liquid water containing bulk NBs and also in the interfacial tension between oil and NB enriched water. Although bulk NBs, alone, have no effect on surface and interfacial tension, they do present surface activity when they are combined in aqueous solutions with the appropriate surfactants.

Surfactants are amphiphilic molecules that, when present at low concentration in a system, have the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces[13]. Surfactants can be anionic, cationic, non-ionic or zwitterionic depending on the nature of the hydrophilic group. In particular, anionic surfactants have a negative charge on their hydrophilic end while cationic surfactants have a positive charge respectively. Zwitterionic or amphoteric surfactants carry both positive and negative charge. Surfactants are also classified in water-soluble and water-insoluble. The interaction between NBs and surfactants have been studied by many researchers[14]–[20]. According to these studies, the presence of bulk NBs significantly reduced surface tension in an anionic surfactant solution. On the contrary, no considerable change in surface tension was observed in cationic and non-ionic surfactant solutions, in the presence of bulk NBs.

The addition of different types of surfactants (anionic, cationic, non-ionic) on NB suspensions, present different effect in the value of NBs zeta potential. In particular, non-ionic surfactants have no effect while cationic surfactants decrease the magnitude of the negative value of NBs surface potential due to the adsorption of the cationic group, leading to reduction of NBs stability. On the other hand, the addition of anionic surfactants like Sodium Dodecyl Sulfate (Fig. 3) causes an increase in the magnitude of the negative value of NBs zeta potential as shown in Fig.4. The anionic surfactant molecules adsorb on the NBs interface with the anionic group orientating itself towards the liquid phase whilst the hydrophobic tail orientates itself towards the gas phase^[16] enhancing the stability of the nanobubbles by the so-called electro-steric stabilization mechanism as the surface charge increases with surfactant concentration. Thus, the stability of the NBs increases and the electrostatic repulsion forces become stronger. It can be stated that the observed SDS interfacial behavior in the presence of nanobubbles can be attributed to the electrostatic repulsive interaction, leading to the increased surfactant surface activity and the lower surface tension values. The aforementioned observed decrease in the surface tension can be attributed to these forces as presented in Fig.5. The presence of NBs in the anionic surfactant solution, enhances the adsorption of surfactant molecules in air-water interface and consequently decreases the surface tension. This complex system of anionic surfactant-

nanobubble functions as a novel surface-modifying agent that can potentially be used for stabilizing disperse systems such as foams and emulsions. This process could be advantageous for industries like oil & gas industry, food industry, cosmetic industry, wastewater treatment, surface cleaning and medical applications where surfactant technology is extensively applied.

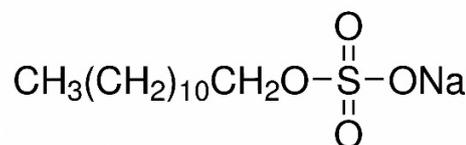


Fig. 3. Sodium Dodecyl Sulfate (SDS; cmc = 8.2 mM)

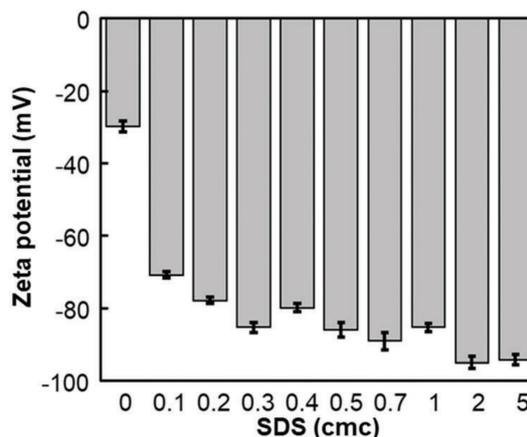


Fig. 4. Effects of addition of Sodium Dodecyl Sulfate in aqueous NB suspension^[16].

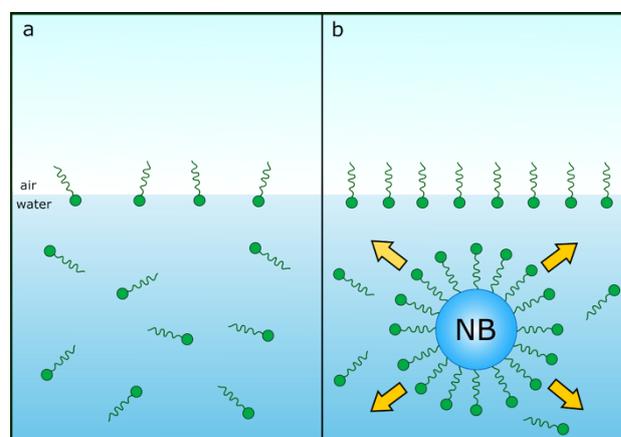


Fig. 5. Anionic surfactant solution without NBs (a) and with NBs (b). The presence of NBs in the anionic surfactant solution, enhances the adsorption of surfactant molecules in air-water interface due to electrostatic repulsion forces and consequently decreases the surface tension.

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