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Water/oil/water thin films: construction and applications

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Abstract With the classical “thin-film balance” apparatus, one can study the properties of thin soap films (air/water/air films). Here, we present a new version of that apparatus allowing us to build a single thin oil film horizontally held on a frame and completely immersed in water. The frame used here is a glass frit: to make it suitable for holding oil films in water and to overcome wetting problems, we have developed a special surface treatment by silanization of the frit. With that device, we can directly and simultaneously control, change and measure both the film thickness and the disjoining pressure in these

water/oil/water films. Related to structural, dynamical and stability issues, the range of studies and applications is wide with the new experimental configuration. We present experimental tests on the validity of the setup, also showing typical thickness instabilities which appears to be important in these kind of films. We also discuss information provided on the stability of thin liquid films in liquid–liquid extraction problems.

Key words Thin liquid films · Inverse emulsion · Liquid–liquid extraction · Thickness instability · Disjoining pressure

Introduction

Liquid–liquid extraction techniques are used for specific treatments of nuclear wastes. Appropriate molecules can selectively extract ions from complex solutions. In the industrial DIAMEX process, an oil solution of an extractant molecule (dimethyldibutyltetradecylmalonamide) is mixed with an aqueous solution containing the ions to extract [1]. The mixing process, creating an inverse emulsion (water in oil), results in the transfer of the ions from the aqueous phase to the oil one. The properties of the organic phase have recently been studied [1]. It turns out that it can be considered as a micellar solution of the extractant molecules, and that many features of the process can be explained through that picture. However, only little is known on the emulsion itself and on the mechanisms and dynamics of the transfer. Studying the stability and the properties of the water/oil/water (w/o/w) thin films separating two

water droplets (where ion transfers mainly occur) is thus very interesting since it can provide new information on the emulsion microscopic structure and on the possible role and organization of the micelles in these films. Foam surfactant films have been studied extensively, especially with the thin-film balance (TFB) [2]. There are also numerous studies on pseudoemulsion films (oil/water/air films) and on emulsion films (oil/water/oil, o/w/o films) [3–8]; however, surfactant films of oil in water have almost never been studied in terms of disjoining pressures, π (force per area unit between the interfaces), versus film thickness, h . Only recently, a study of decane and polymeric surfactant films in water was reported [9]. In order to investigate w/o/w films, and especially those involved in the liquid–liquid extraction DIAMEX process, we have developed a new version of the TFB, which allows us to control and change the film thickness and to directly measure disjoining pressures.

Adapting the classical TFB method

The classical TFB allows the study of a single thin foam film, held horizontally on a support [2]. The support is a glass frit, and the film is made inside a small hole (diameter of 1–2 mm) in the frit. The frit is placed in a closed box where the internal pressure can be increased in order to apply normal forces on the film and to change its thickness (measured by interferometry). The frit, acting like a reservoir for the film, is connected to a reference pressure by a capillary tube. It is thus possible to get $\pi(h)$ curves as well as direct film observations by videomicroscopy. The main issue for adapting the classical TFB to make w/o/w films concerns the film holder. Glass frits are naturally hydrophilic; thus, if one tries to put such a frit full of oil in water, oil comes out of the frit and is replaced by water, and the experiment cannot be performed correctly. This technical problem is maybe one of the reasons why w/o/w films have not been studied so much. Our major breakthrough has been to develop a chemical treatment (silanization) of the frit to make it hydrophobic. Alkyl trichlorosilane molecules can covalently bind to the frit surface, making it hydrophobic via the grafted alkyl chains. In order to obtain the treatment inside all the frit pores, the silanization has to be done in the gaseous phase of the silane solution (using short alkyl chains, like C6 or C8) inside a sealed box under vacuum. This provides highly hydrophobic frits which, once full of oil, can be dropped in water without any problems. Other important improvements have been necessary in the setup: use of an immersion objective, installation of a suction system for changing the film thickness. Details can be seen in Fig. 1. Also, procedures have been developed, involving microsyringes, for the initial positioning of an oil droplet in the frit hole with water below and above it.

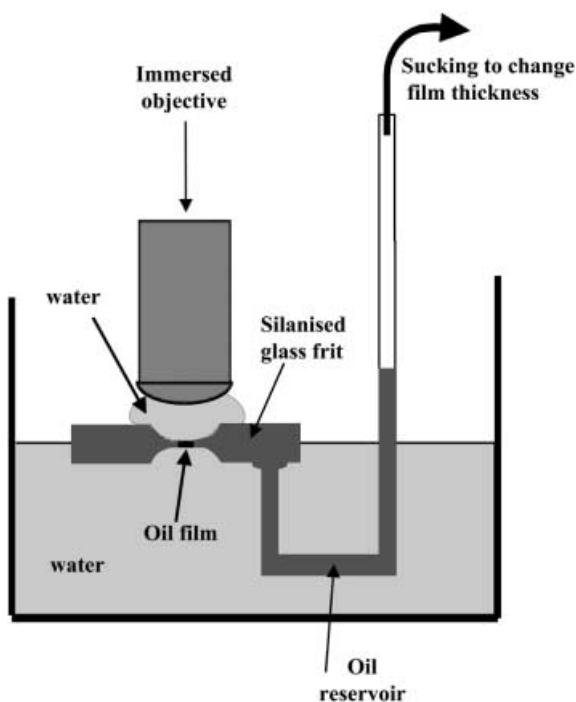


Fig. 1 Setup for water/oil/water thin films. The glass frit became hydrophobic by silanization

Results

We first tested our setup with the same system as in Ref. [9]: decane (or dodecane) and ABIL EM-90 films in water. ABIL EM-90 is a large comb copolymer known for strongly stabilizing inverse emulsions. It has a rigid poly(dimethylsiloxane) backbone with hydrophobic alkyl and hydrophilic ethylene/propylene oxide grafts. The molecular weight is 62,000 for the purified product. Note that neither the molecular weights of the various groups nor their distribution on the backbone is known.

Highly stable films have been observed and a $\pi(h)$ curve measured (Fig. 2). This curve is in good agreement with that in Ref. [9]. Note that in Ref. [9], disjoining pressures were not obtained directly, but via conductivity measurements. Here, the pressures are simply extracted from a manometer in the suction system. As already said in Ref. [9], understanding the microscopic structure within the film (with regard to the measured thickness) is not easy since the molecule structure is not well known; however, such measured thickness are consistent with the alkyl chains elongated orthogonally to the surface. With these films, we detected a spontaneous cyclic instability of the thickness (Fig. 3). The mean thickness rapidly decreases to around 10 nm in a few seconds, while many small droplets get trapped in the films (dimples). These dimples grow and coalesce; finally the initial thickness is recovered. The mechanism of this instability is not yet understood, but it can probably be connected to the observations of “cyclic dimpling” seen in direct emulsion films [7]; a phenomenon explained both by surfactant redistribution between the phases and by Marangoni effects.

We also tested a smaller and simpler molecule: SPAN80 (monooleate sorbitan) in dodecane. This is also

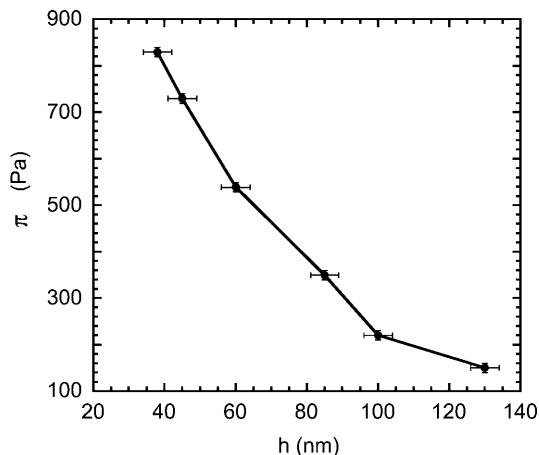
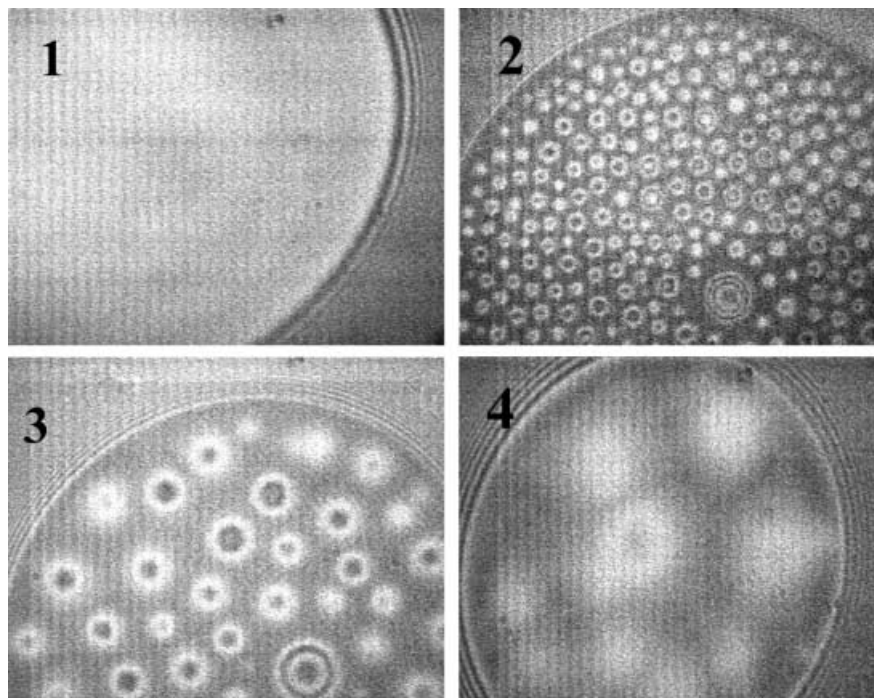


Fig. 2 Disjoining pressure versus film thickness for a dodecane and ABIL EM-90 film in water

Fig. 3 Spontaneous and cyclic thickness instability in a dodecane and ABIL EM-90 film in water. After step 4, the homogeneous film, as in step 1, is recovered



a well-known system for making stable inverse emulsion. Once again, very stable films were observed, showing a dynamical thinning by layers of micelles at a high concentration of SPAN80 and a single transition to a very thin black film at low concentration. Note also that all these w/o/w films show strong dimpling instability in their formation: a large amount of liquid can be trapped in the center of the film, inducing a nonflat film shape. This hydrodynamic effect means that the velocity of the film opening (describing how fast a droplet spread on another one) is much higher than the draining one within that film. Initial dimples also occur in foam films, but they usually disappear in a few seconds, while here they can last for minutes (and can eventually lead to the rupture of the films).

Finally, we studied the dodecane and extractant films in water. Thin films can be formed, but whatever the concentration of extractant used (0.05–1 M) and the temperature, no stable films can be found. The films also show strong initial dimpling. In the case where dimples escape out of the film, the films reach a flat shape and gently thin to a typical rupture thickness of 50 nm (Fig. 4). Again, this rupture thickness does not seem to depend on the extractant concentration. However, the thinning dynamics depends on it and on the temperature (Fig. 4). Actually, the more viscous the solution, the slower it drains. Just before rupture and for the thinnest films, some darker domains in the films are often seen (for high extractant concentration), indicating a thickness jump owing to structuralization of micelles near the surface (the measured thickness of the jump roughly

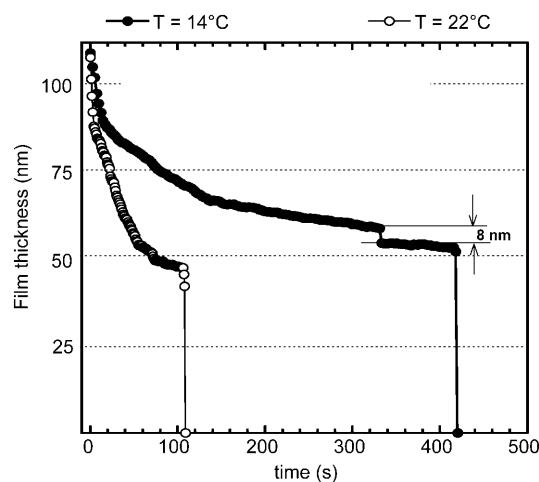


Fig. 4 Thinning dynamics for a dodecane and extractant film in water. An increase in extractant concentration produces the same features as a temperature decrease

corresponds to the calculated distance between the micelles, Fig. 4).

Conclusions

We have developed a new version of the TFB for studying thin oil films in water. The major improvement is related to the inversion of the wetting properties of the frit. Tests have shown that for systems, known for

making stable inverse emulsions, stable thin films are observed. This new setup is the first, to our knowledge, that allows the complete study of this type of film. Note that with this setup, we are able to visualize thin oil films of only a few nanometer thickness in water, while the refractive index of water and oil are almost identical and we are able to measure forces between liquid interfaces separated by oil. The results also show that for these types of films, involving liquid–liquid interfaces, the film shapes can be complicated and can be unstable. This is different from foam films, where higher surface tensions make more flat surfaces. Coupling studies of w/o/w and o/w/o films could probably give new insight into the hydrophile–lipophile balance scale

at this thin film level. Regarding the liquid–liquid extraction process, we have obtained new information on the emulsion structure. It turns out that the w/o/w thin films are always unstable. In this way, the ion transfer appears to be facilitated by continuous creation and destruction of interfaces and films, in order to have a high actual exchange surface. Thus, the important parameters appear to be the life time of the film and its typical range of thickness. Efficient extractant molecules should not make very stable emulsions, but should not make fast droplets coalescence either. Also, the typical thickness is that where extractant micelles get confined near the interfaces, showing that the transfer can be enhanced by this confinement.

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