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Fluorosurfactants for microdroplets: Interfacial tension analysis

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ABSTRACT

Quantitative analysis of a number of potential fluorous surfactants, prepared with a view to stabilisation of microdroplets in microfluidic systems is presented. The surfactants tested comprised compounds with both perfluoropolyether (PFPE) and perfluoroalkyl (PFA) tails, along with three classes of hydrophilic head group, including crown ethers and hexaethylene gylcol. Surfactants were tested for activity using the pendant drop technique. Six compounds proved highly effective and efficient surfactants, with γ_{CMC} < 10 mN/m and CMCs in the sub-millimolar range. These six compounds stabilised aqueous microdroplets in fluorous oils within poly(dimethylsiloxane) (PDMS) microdevices to a greater degree than commonly used pseudosurfactants such as perfluorooctanol.

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1. Introduction

Recent advances in the field of microdroplets have demonstrated the ability to stabilise water droplets within a stream of fluorous oil via the presence of effective fluorosurfactants in the oil phase [1,2]. Such a development is welcome, as it permits the advantages of the microdroplet field – monodisperse droplet formation, high rates of droplet generation and small sample volume requirements, among others [3,4] – to be applied to biological testing and chemical synthesis via commonly used fluorous continuous phases [5–9]. However, this ability to create highly stable water microdroplets has not yet been accompanied by a detailed investigation of the nature of the interaction between the surfactant and water and oil phases in the microenvironment. Underpinning this technological innovation by a quantitative characterisation of the fundamental interactions behind such an application – in this case, molecular interactions and interfacial energies – would be beneficial to all practitioners in the field, leading to greater maturity in the future appropriation of such technology.

This paper presents a quantification of the properties of several potential fluorosurfactants, synthesised for use within a microfluidic environment, and correlates these properties with their ability to stabilise the fluorous oil–water interface within such an environment. While literature on both the synthesis and analysis of fluorous surfactants is vast [10–16], studies combining an analysis of surfactant properties with a demonstration of their application to microfluidics are rare. It is this lacuna that this paper aims to fill, in the hope that this will further the understanding of the interactions between surfactant and liquid phases, and permit the future creation of more effective surfactants.The surfactants discussed in this paper are shown to be effective in generating stable water droplets within streams of fluorous oil in PDMS microfluidic devices, and their surfactant properties compare well with studies on similar molecules.

2. Materials and methods

2.1. Measuring potential surfactant performance

Potential surfactant molecules require a quantitative characterisation of their ability to stabilise a given liquid–liquid interface. This can be achieved via measurement of interfacial tension (IFT, γ), at the interface to gain insight into the dissimilarity between the two phases, and the degree to which the presence of surfactant organises the interface of two immiscible liquids.

In order to translate this quantitative measure into an indicator of the degree to which a given surfactant enables droplet formation within a microfluidic device, such quantitative characterisation must be correlated to a qualitative assessment of surfactant efficacy towards forming and stabilising droplets within a microfluidic environment. This can be accomplished by observation of the fluid flow regimes within which a given concentration of surfactant enables droplet formation in a microfluidic environment. For the purposes of the present work, it will be sufficient to initially demonstrate a correlation between low γ_{CMC} and successful droplet formation for fluorosurfactants.

Quantitative surfactant assessment begins with ensuring the correct hydrophilic–lipophilic balance (HLB) is present in the surfactant, so that the correct emulsion is formed [17,18]:

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$$HLB = 20 \times \frac{H_w}{H_w + L_w} \quad (1)$$

where H_w is the molecular weight of the hydrophilic portion of the molecule, and L_w the molecular weight of the hydrophobic portion of the molecule.

The HLB gives a rough estimate of the performance of a surfactant on an arbitrary scale between 0 and 20. A value near zero indicates a completely lipophilic molecule, and a value near 20 indicates a completely hydrophilic molecule. In order for a water-in-oil emulsion to be formed, the hydrophobic tail of the surfactant must be of greater molecular weight than the head group [18]. A value of less than ten is required for the correct water-in-oil emulsion formation within a microfluidic environment. Surfactant performance may be further examined quantitatively by measurement of the effectiveness and efficiency of a surfactant in reducing the interfacial tension at a given interface [19].

Surfactant effectiveness can be measured in terms of the minimum IFT achievable (γ_{CMC}) between two liquid phases in the presence of the surfactant, and the surfactant concentration at which the IFT reaches a minimum (CMC) [19]. Consideration of the change in IFT with surfactant concentration also gives Π_{CMC}, the value by which IFT is reduced at the CMC relative to a surfactant-free system, as well as a further measure of surfactant effectiveness, pC_{20}:

$$pC_{20} = -logC_{20} \quad (2)$$

where C_{20} is the surfactant concentration which reduces IFT by 20 mN/m, relative to a surfactant-free system.

Surfactant efficiency is indirectly related to the closeness of surfactant packing at the interface between the two phases. The degree of surfactant packing can be obtained by solving the Gibbs equation for the surfactant surface excess concentration for non-ionic surfactants in dilute ($<10^{-2}$ M) solutions [19]:

$$\Gamma = -\frac{1}{2.303RT}\frac{d\gamma}{dlogC} \quad (3)$$

where Γ, the surface excess concentration, can be calculated from the maximum slope of the plot of interfacial tension versus logarithmic surfactant concentration. This maximum slope frequently occurs at surfactant concentrations close to C_{20}. The surface excess concentration can then be used to give the area occupied by the surfactant molecule at the interface, a (4):

$$a = \frac{1}{\Gamma N} \quad (4)$$

where N is Avogadro's constant.

The desired criteria for fluorosurfactants within microdroplet environments are outlined below.

2.2. Surfactant performance criteria

To form microdroplets within PDMS devices, the IFT of a fluorous oil/water mixture must be below 20 mN/m, lowered from a surfactant-free IFT of around 55 ± 2 mN/m. The threshold of 20 mN/m is selected to be similar to the γ_{CMC} of perfluorooctanol (PFO) (15 mN/m), a pseudosurfactant, which can form meta-stable water droplets in fluorous oil when used in volume ratios of 10–30% with a fluorous oil (such a Fluorinert FC-77, 3M) [7,6]. Fluorinert FC-77 (3M), comprising several low molecular weight fluorous ethers,[2] is frequently used as the fluorous oil phase in microdroplet devices [7]. Such droplets within an FC-77/PFO system are prone to coalescence upon contact with each other. For greater stability, a lower CMC will be preferred, leading to a requirement of $CMC < C_{20}$. A surfactant effectiveness of $\gamma_{CMC} < 20$ mN/m is then the first requirement for a suitable candidate for microdroplet formation.

A suitable surfactant will also have a CMC in the millimolar range (examples of experimentally determined limits used in this investigation are, $<10^{-2}$ M to ensure complete solubility of the surfactant in the oil phase, $>10^{-5}$ M to ensure that there is sufficient amounts of surfactant in the oil such that the water–oil interface is quickly saturated with surfactant and the interfacial tension minimised). A lower CMC will of course lead to a lower concentration of surfactant in the oil required to reduce IFT below the chosen threshold. However, this must be balanced against the requirement to achieve a stabilised oil–water system as rapidly as possible for stable droplet formation within microfluidic devices. The rate at which the system is stabilised by the surfactant depends upon the rate at which surfactant is adsorbed at the interface. This in turn is dependant upon the amount of surfactant present at the system and the mobility of that surfactant with respect to organisation at the oil–water interface. Interface stability is related to the interfacial area occupied by the surfactant: a surfactant that packs more regularly at the interface for a given concentration will provide greater stability of that interface relative to a surfactant that packs less tightly at the interface [19]. Surfactant efficiency is therefore required to be as great as possible (high values of Γ and concomitantly low values of a), providing that CMC falls within acceptable concentration ranges.

2.3. Chemical synthesis

The structures of the surfactants tested are shown in Fig. 1. The surfactants comprise either a perfluoroalkyl (PFA) or perfluoropolyether (PFPE) tail with a variety of head groups. Carbohydrate groups were used to create molecules **1–5**: **1** contains keto–L-gulonic acid, **2** contains D-glucose, **3** contains D-galactose and **4** and **5** contain D-galactos-1-amine. Two different crown ether head groups were included in molecules **6–9**: aminomethyl 15-crown-5 in **6** and **7** and aza-18-crown-6 in **8** and **9**, while hexaethylene glycol was used to create molecules **10–12**. Detailed synthetic information on the fluorosurfactants tested in this work will be published elsewhere.

2.4. Interfacial tension measurement via pendant drop

Measurement of the interfacial tension between the oil and aqueous phases was accomplished outside of a microdroplet environment by using the pendant drop technique [20–23], chosen because of the small amount of sample required for measurements. Measurements were made using a custom-built syringe pump and camera apparatus (see Supporting Information). Oil-surfactant solutions were extruded from a 0.8 mm OD flat-tipped needle into a cuvette of deionised water (Millipore milliQ QGard 1) and photographed at the point of detachment from the needle (Fig. 2). Interfacial tension values were extracted from the photographs using Image-J software (NIH) [24] via standard methods [21–23]. The resulting data were fit to curves of the form $y(x) = \alpha.exp(-\beta.x) + \eta$, where the coefficients α, β and η were found using a weighted algorithm in Matlab. The IFT of a 30% w/w solution of perfluorooctanol in FC-77 was measured to be 14.7 ± 0.4 mN/m, which closely compares to literature values for similar systems [5,25].

2.5. Creation and observation of droplets in microfluidic devices

Quantitative interfacial tension data from the pendant drop analyses were correlated to a qualitative test of the performance of the surfactant by formation of aqueous microdroplets within a

[2] FC-77 is a mixture of C_7F_{16} and $C_8F_{16}O$ in a batch-dependant ratio, with boiling point 100 °C and density, ρ = 1.78 g/cm^3.

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